Universidade de Aveiro Departamento de Química
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Ana Margarida Martins Salgueiro Carta

Utilização do processamento a alta pressão na modificação das propriedades físicas e sensoriais de papéis *tissue*

Use of ultra-high pressure on the modification of physical and sensorial properties of tissue papers

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Dissertação à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Engenharia Química – Especialização em Engenharia de Materiais e Produtos Macromoleculares, realizada sob a orientação científica do Doutor Dmitry Evtyugin, Professor Associado com agregação, Doutor Jorge Saraiva, Investigador Auxiliar, do Departamento de Química da Universidade de Aveiro e com o auxílio do coordenador empresarial Doutor Filipe Almeida, Diretor técnico da empresa Renova FPA -S.A.

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Dedico este trabalho à minha Mãe e ao meu esposo pelo apoio incansável.

o júri

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keywords

High pressure, celulose, virgin pulp, recycled pulp, hornification, hydration, impregnation, additives

abstract

The ultra-high hydrostatic pressure processing (UHP) is an expanding technology used mostly in food industry for the pasteurization of foods while preserving their organoleptic properties. This technique may be also applied to introduce structural and functional changes in biomolecules including cellulose. Recent studies have demonstrated the potential of UHP towards cellulosic pulps, namely the ability to promote forced fibre hydration thus improving cellulose accessibility and fibrils reorganization. The main purpose of this thesis was the evaluation of UHP potential for the modification of recycled fibres aiming to improve its performance in the production of tissue paper in collaboration with the biggest national producer Renova FPA, S.A.

The present study has identified the structural changes that occurred in cellulose of recycled pulp induced by UHP. Thus the crystalline regions demonstrated to some extent the co-crystallization of appropriately oriented crystallites and the recrystallization of paracrystalline regions as demonstrated by XRD and ^{13}C NMR. In addition, UHP have induced fibrils disaggregation upon forced hydration thus enhancing their accessibility towards water and chemical reagents. A substantial reduction of recycled fibres hornification upon UHP has been suggested. UHP-processed recycled fibres also demonstrated the increment of strongly bound water content, as revealed by thermal analysis and by FTIR of deuterated samples. Changes in physical structure of cellulose caused the enhancement of such properties of recycled pulp as accessibility, hydrophilicity, moisture sorption capacity, surface contact angle, capillarity, among others.

The effect of beating (B) before (B-HP) or after the UHP (HP-B) or between two beating stages (B1-HP-B2) on the drainability and mechanical properties were evaluated. In these studies, basic papermaking properties and, especially, the capillarity (up to 112%) were improved. The most advantageous from the point of view of strength properties of tissue paper production was suggested to be the B1-HP-B2 sequence suitable both for recycled fibres and softwood fibres. A synergetic effect of UHP on the beating of recycled cellulosic fibres has been detected allowing up to 50% energy savings in refining. At the same time, the UHP effect on the virgin fibres refinability was much more moderated.

The enhanced accessibility of recycled pulp upon UHP was also used to improve its ability towards targeted chemicals, enzymes and nano-sized structures. These experiments were carried out also with dried virgin fibres used as the models of recycled pulp. As concerns enzymes, it was suggested that enzymatic modification improves significantly the papermaking properties of recycled pulp. These improvements were related with selective removal of xylan bound to impurities and to aggregated cellulose fibrils on the fibre surface thus favouring the ensuing swelling and inter-fibre bonding in paper. UHP pre-treatment and posterior enzymatic treatment revealed a synergetic effect on the mechanical properties of recycled pulp. This fact was assigned to enhanced accessibility of fibres towards xylanase by forced hydration and favourable rearrangement of cellulosic fibrils in fibres after UHP pre-treatment. The increase of basic strength properties after UHP and promoted by xylanase treatment was up to 30%, being the most pronounced for the tensile strength and the burst resistance.

The impregnation of dyes in combination with UHP also has demonstrated an enhancement in impregnation/fixation of dye molecules. However, a high dependence was found on the equilibrium between dye, fixative and cellulosic fibres, depending on the dye used, both with and without UHP. This behaviour was assigned to specificity of dyes molecular structure, affinity, substantivity, among others.

The impregnation of humectant compounds applying UHP was also evaluated and the improved hygroscopicity of treated pulp was confirmed. This fact was evidenced by capillarity, water absorption capacity and moisture sorption tests.

The effect of UHP on the impregnation of antimicrobial agent in fibres has been carried out using polyhexamethylene biguanide (PHMB). Being a cationic polymer, PHMB was readily absorbed in fibres with and without UHP treatment. However, UHP allowed higher PHMB uptake and better retention after leaching when compared to conventional impregnation without UHP. This was attributed to stronger interactions between cationic PHMB and cellulose due to the deeper penetration of the antimicrobial agent under UHP treatment. However, the amount of PHMB to impregnate in fibres is limited because of its negative effect on paper strength properties due to disruptive action of PHMB as debonding agent.

Likewise, silica encapsulated PHMB demonstrated fairly high retention upon UHP and high release during the leaching tests. Being encapsulated, PHMB was not directly bound to cellulose (electrostatic interaction) and the final paper showed at the same time fairly high PHMB release rates.

The impregnation with encapsulated perfumes (*Dovena New*) was also carried out and revealed higher impregnation of these nano-sized structures upon UHP than under conventional conditions. This was reflected by a higher release of volatiles from pulp samples impregnated with stuffed nanoparticles under UHP treatment when compared to pulps samples with free adsorbed nanoparticles.

Palavras-chave

Alta pressão, celulose, pasta virgem, pasta reciclada, hornificação, hidratação, impregnação, aditivos

Resumo

O processamento de alta pressão hidrostática (UHP) é uma tecnologia em expansão, bastante utilizada na indústria alimentar para a pasteurização de alimentos, ao mesmo tempo que preserva as suas propriedades organoléticas. Esta técnica pode ainda ser aplicada na modificação estrutural e funcional de biomoléculas, tais como a celulose. Em estudos recentes demonstrou-se o potencial da UHP para com pastas celulósicas, nomeadamente no que diz respeito à sua capacidade de promover a hidratação forçada das fibras e, consequentemente, melhorar a acessibilidade das mesmas e ainda promover a reorganização das suas fibrilas. Posto isto, o principal objetivo desta dissertação consistiu na avaliação do potencial da UHP na modificação de fibras recicladas e virgens, para alcançar a melhoria da sua *performance* na produção de papéis *tissue*, em colaboração com uma das maiores empresas nacionais do ramo, a Renova FPA, SA.

No presente estudo foram identificadas alterações estruturais na celulose, tanto em fibras recicladas como em virgens, produzidas pelo UHP. Neste sentido, as regiões cristalinas demonstraram, até certa extensão, a co-cristalização de cristalitos convenientemente orientados e a recristalização de regiões paracristalinas, tal como evidenciado por XRD e ^{13}C RMN. Para além disso, a UHP induziu ainda a desagregação das fibrilas, aquando o fenómeno de hidratação forçada, originando maior acessibilidade à água e a reagentes químicos. Sugere-se ainda a ocorrência de uma redução significativa da hornificação das fibras. Fibras processadas por UHP também demonstraram um incremento na presença de água fortemente ligada, tal como sugerido por análises térmicas e FTIR de amostras deuteradas. As alterações produzidas na celulose originaram uma melhoria nas propriedades das fibras, nomeadamente da sua hidrofilicidade, sorção de vapor de água, ângulo de contacto de superfície, capilaridade, etc.

O efeito da refinação (B) antes (B-HP), ou depois da UHP (HP-B), ou entre refinações (B1-HP-B2), também foi analisado no que diz respeito à drenabilidade e propriedades mecânicas das fibras. Nestes estudos, as propriedades papeleiras e em especial a capilaridade (112%) revelaram melhorias. Com base nos resultados sugere-se que a sequência B1-HP-B2 seria a mais vantajosa para fibras recicladas e fibras virgens longas. Para além disso, o efeito sinergético da UHP com a refinação sugere ainda a possibilidade de uma poupança de 50% de energia na refinação.

As melhorias induzidas pela UHP na acessibilidade de fibras celulósicas foram também utilizadas para otimizar a impregnação de químicos, enzimas e nanoestruturas. No que diz respeito às enzimas, verificou-se que a modificação enzimática de fibras celulósicas promoveu melhorias significativas nas propriedades papeleiras destas, em especial das fibras recicladas. Estes resultados foram relacionados com a remoção seletiva de xilana ligada a impurezas e a fibrilas na superfície das fibras, que consequentemente favoreceu o intumescimento e a ligação entre fibras.

A utilização de um pré-tratamento de UHP e um posterior tratamento enzimático revelaram um efeito sinergético nas propriedades mecânicas das fibras celulósicas, em especial nas fibras recicladas. Este facto foi relacionado com o aumento de acessibilidade nas fibras para com a xilanase, como consequência da hidratação forçada e rearranjo favorável das fibrilas originado pela UHP. A melhoria registada nas propriedades mecânicas das fibras, como resultado do pré-tratamento UHP e posterior tratamento enzimático, foi até 30%, tendo demonstrado maior impacto nas propriedades de índices de tração e rebentamento.

A impregnação de corantes com UHP também foi realizada e demonstrou uma melhor impregnação/fixação das moléculas de corante. No entanto, verificou-se uma grande dependência no equilíbrio entre moléculas de corante, fixador e fibras celulósicas, dependendo no corante utilizado, com e sem alta pressão. Estas variações foram atribuídas à especificidade da estrutura molecular da molécula de corante, à sua afinidade, substantividade, etc.

A impregnação de agentes humectantes com UHP também foi avaliada e a melhoria nas propriedades hidrofílicas de fibras celulósicas foi confirmada. Este facto foi evidenciado por testes de capilaridade, sorção de vapor de água e testes de capacidade de sorção de água.

O efeito da UHP na impregnação de um agente antimicrobiano também foi estudado utilizando polihexametileno biguanide (PHMB). Sendo um polímero catiónico, o PHMB foi facilmente absorvido pelas fibras celulósicas, com e sem alta pressão. A UHP permitiu ainda uma melhor impregnação/retenção do PHMB, após lixiviação, quando comparado com a amostra impregnada sem UHP. Estes resultados foram relacionados com as fortes interações estabelecidas entre o PHMB catiónico e a celulose, devido a uma impregnação mais profunda do agente antimicrobiano durante o tratamento de UHP. No entanto, o teor de PHMB a impregnar nas fibras é limitado pelos efeitos negativos que este originou nas fibras como consequência da sua ação de interrupção das ligações entre fibras como “agente desligante”.

Do mesmo modo, cápsulas de sílica com PHMB também demonstraram uma maior retenção nas fibras celulósicas com a utilização da UHP. Encapsulado, o PHMB não está diretamente em contacto com a celulose (interações electroestáticas), exibindo deste modo uma maior libertação de PHMB (limitação por difusão).

A impregnação com perfumes (Dovena New) encapsulados também foi realizada e revelou uma maior impregnação destas nanoestrutras, com a utilização da UHP, relativamente à metodologia convencional. Isto foi refletido pela maior libertação de voláteis por parte das amostras impregnadas com cápsulas com perfumes.

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Abbreviations and Symbols

4-*O*-Me-GlcA	4-O-methylglucuronic acid
A	constant from Halsey, Henderson, Oswin and Smith model
A_m	Effective cross-section area of adsorbate
a_w	water activity
AGU	anhydroglucose unit
Araf	arabinofuranose
Ara	arabinose
AUX	activity arbitrary units of xylanase
b	average height of cellulosic crystalline cell
B	constant from Henderson and Oswin model stage
BET	Brunauer–Emmett–Teller model
c	concentration
C	chlorine bleaching stage
C	constant from BET and GAB model
C_0	constant from temperature dependence of constant C
CA	contact angle
CD	crystallinity degree
CIE	Comission Internationele de L'Eclairage
COD	chemical oxygen demand
CTAB	hexadecyltrimethylammonium bromide
CTMP	chemi-thermo-mechanical pulp
CWP	conventional wet pressing process
D	chlorine dioxide bleaching stage
D_{200}	Average crystallite width from plane 200
DN	Dovena New fragrance
DNS	3,5-Dinitrosalicylic acid
DSC	Differential scanning calorimetry
E	extraction stage on bleaching
ECF	elemental chlorine free
EDA	ethylenediamine
EDTA	ethylenediaminetetraacetic acid
FAS	formamidine sulphinic acid
FOL	fixative optimum load
FTIR	Fourier transform infrared

g	acceleration due to gravity
GAB	Guggenheim-Anderson-de Boer
Galp	galactopyranose
Glc	glucose
Glcp	glucopyranose
GlcpA	glucuronic acid
h	capilary rise
H	sodium hypochlorite bleaching stage
HDPE	high-density polyethylene
HPLC	high performance chromatography
HP-B	sequence of ultra-high pressure followed by a beating stage
HPP	high pressure processing
HHP	high hydrostatic pressure
K	GAB constant
k_0	constant from temperature dependence of constant K
k_1	PELEG constnat
k_2	PELEG constant
M_w	molecular weight
Manp	mannopyranose
ML	middle lamella
MOW	mixed office waste
N_a	avogadro number
NMR	nuclear magnetic resonance
O	oxygen bleaching stage
OBA	optical brightening agent
OCC	old corrugated containers
OMG	old magazines
ONP	old newsprint
P	hydrogen peroxide bleaching stage
P	primary wall
PGW	pressure groundwood pulping
PHMB	polyhexamethylene biguanide
PP	sodium polyphosphates
q_1	partition function of molecule in monolayer
q_l	partition function of molecule in bulk liquid

q_m	partition function of molecule in multilayer
Q_s	Total heat of sorption
r	Halsey constant
r	radium of a capillary
RH%	relative humidity percentage
RMP	refiner mechanical pulping
S	specific surface area
S_1	outer secondary wall
S_2	middle secondary wall
S_3	inner secondary wall
SGW	stone groundwood pulping
TAD	through air drying technology
TCF	totally chlorine free
TEOS	tetraethyl orthosilicate
TMP	thermos-mechanical pulping
TOC	total organic compounds
UHP	ultra-high pressure
VOC	volatile organic compounds
xyl	xylose
X	enzymatic stage on bleaching
X_{eq}	moisture sorption at equilibrium
X_m	monolayer estimate from BET and GAB model
XRD	x-ray diffraction
Xylp	xylopyranose unit
Z	ozone bleaching stage

θ	contact angle between liquid and capillary surface
θ	Halsey constant
γ	surface tension
ρ	density
ΔH_C	difference in enthalpy between monolayer and multilayer
ΔH_k	difference in enthalpy between bulk liquid and multilayer
ΔH_s	net isosteric heat of sorption
ΔH_v	evaporation enthalpy of water
$\Delta H_{s,t}$	theoretical estimate of the net isosteric heat of sorption

Ψ_0 surface potential

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Chapter I

Introduction

Contents

1.1. Introduction

Tissue products market is the fastest growing market among industrially produced papers.[1,2] Examples of tissue papers include toilet paper, kitchen towels, napkins, facial tissue paper, etc. All these products have been demonstrating increasing demand in modern societies, as diary used products for personal hygiene, and also in numerous domestic or industrial applications.

Similarly to other industries, an effective and sustainable development are in the focus of tissue paper producers. This is particularly true for Renova a renowned Portuguese tissue paper producer. Renova is known not only for its high quality soft, absorbent tissue papers but also by its innovative products, such as black and strongly coloured toilet papers and napkins or facial papers with special features.

For the manufacture of tissue paper, Renova uses a wide variety of pulp sources. These include primarily long (softwood) and short (hardwood) "dried virgin" fibres, but also a wide range of recycled fibres (from printed to packing papers). The tissue papers from Renova contain up to 70-80% recycled fibres. Yet, recycled fibres utilization still exhibits some major drawbacks, relatively to virgin fibres, which imply the addition of virgin fibres to surpass those limitations and maintain basic papers properties. Among the negative factors affecting recycled pulp properties, the hornification effect is recognized as the main responsible for recycled fibres losses (losses on physical and mechanical properties and on fibres hydration abilities). [3–10]

Studies previously carried out at the University of Aveiro have demonstrated the potential of hydrostatic ultra-high pressure to improve cellulosic fibres properties. In these studies it was found that UHP was able to introduce water in inaccessible regions of cellulosic fibrils that resulted in fibril rearrangements, resulting in their higher crystallization degree (larger crystallites), forced hydration (imprisonment of water molecules as strongly bound water), improved accessibility (towards chemicals and enzymes) and as a consequence the reduction of pulps hornification, which limited pulps properties, such as absorbency and mechanical properties.[11–13], which are fairly relevant for tissue papers.

Hence, the technique of hydrostatic ultra-high pressure is a suitable tool to improve properties of recycled fibres towards a new generation of tissue papers.

1.2. Contextualization and Objectives

The main goal of this work was the evaluation of hydrostatic ultra-high pressure, UHP, as a potential tool to enhance tissue paper properties. With this in mind, the main purposes of this study were to investigate the effect of ultra-high pressure on different types of fibres, commonly used by Renova for tissue paper production, recycled fibres and virgin fibres (hardwoods and softwoods) and recycled fibres.

According to results of previous works[11–13], the effect of UHP on Renova feedstock materials, commonly used for tissue productions, was investigated. The UHP effect was evaluated as concerns structural changes of fibres, its capacity towards hydration, fibres accessibility, etc. In this context, high expectation was laid on recycled fibres treatment with UHP.

Since recycled fibres are heavily affected by hornification it was important to evaluate UHP effects on hornified fibres[13,11,12], including their physico-chemical properties heavily affected by hornification. Besides, by reversing hornification the possibility of radical improvement of papermaking properties of recycled fibres in tissue paper production was also investigated.

Besides recycle fibres, UHP effect on "virgin" dried but never used in papermaking pulps was also studied. Such virgin fibres are commonly used in the composition of tissue papers to provide critical properties such as absorbency, softness and adequate mechanical strength.[14–16] The main idea was to verify if UHP treatment could improve the aforementioned pulp properties thus diminishing the dependence of tissue paper composition from virgin pulps. It was expected that under optimized UHP conditions the forced hydration of virgin fibres would provide structural changes favouring their mechanical, optical, adsorption and softness properties.[13] The combination of beating and UHP was also considered to evaluate the effects behind the combination of both treatments.

Taking into consideration that the strategic development lines of Renova are related to the production of strongly coloured tissue papers with specific consumer properties (e.g. highly absorbable, antimicrobial, perfumed, etc), the effect of UHP treatment on the dyeing process and on the accessibility towards various additives (antimicrobial agents, functional nanoparticles, humectants, fragrances and enzymes) was also evaluated.

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Chapter II

Bibliographic Review

Contents

2.1. Cellulosic fibres sources

Cellulose is one of the most abundant polymers in nature. This polymer is found in different terrestrial plants in different amounts, e.g. more than 94% in cotton, 75-80% in hemp, 70-80% in flax, 60-65% in jute and 40-55% in wood. From all these cellulose sources, wood is the most relevant, since it is the main source of cellulosic pulp for papermaking.[1,2]

2.1.1. Macroscopic structure of wood

Wood is composed by a wide variety of tissues cells (Figure 2. 1). When a tree is cut by taking a closer look into its cross-section, from its outside to the inside, it is possible to distinguish different layers, the outer bark, the phloem, cambium, sapwood and heartwood. The outbark confers protection and avoids liquid losses, while phloem is the cells tissue responsible for transporting the nutrients through the plant. In the case of cambium, this layer is responsible for the growth (i.e. cell division, production of xylem and phloem). The new cells inside the cambium become cells in sapwood, and outside cells became cells in the phloem.

Sapwood and heartwood are the tissues responsible for nutrients transport and strength and support, respectively. Xylem (layer created from the cambium to the centre) is the most important part of wood for paper industry. It mainly consists on longitudinal cells, whose primary functions are conduction, support and nutrient storage, as mentioned above. Also, radially oriented cells may be observed. In the xylem, the layers of early and late wood form well visible annual rings.[3–5]

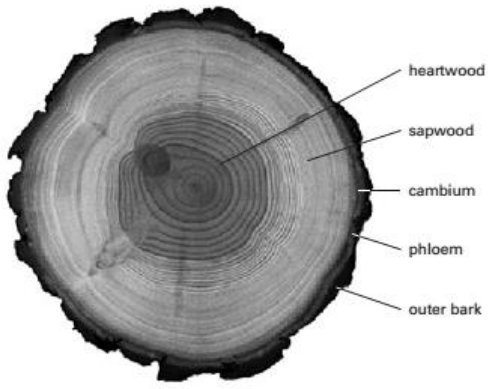

Figure 2. 1 – Transverse cut of a wood stem. [6]

2.1.2. Microscopic structure of wood

Wood cells are not all equal, they differ from tree to tree species. From these differences it is thus possible to divide wood into two types, hardwoods and softwoods.[7,8]

2.1.2.1. Softwood

Softwood belong to coniferous (gymnosperms) and is mainly composed by two types of wood cells, tracheids (90-95%) and ray parenchyma cells (5-10%) (Figure 2. 2).[8]

Tracheids are long cells, featured by its length being much larger than its width. Their functions include mechanical support and water and nutrient transport. The water transport between cells occurs through pits. Being longitudinally orientated, cells exhibit many pits, which enable communication between neighbouring cells.[4,8]

Ray cells are barely visible and appear as lines in a top-to bottom directions. They have approximately 15μm high by 10 μm wide by 150-250μm long in the radial direction. These cells functions include nutrient storage and its lateral transport. Ray cells intercept tracheids, trough pits, which act as communication between cells [4,7]

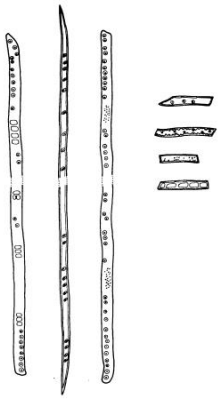

Figure 2. 2 – Typical softwood cells (adapted from [8]).

2.1.2.2. Hardwoods

Hardwood belongs to angiospermes and possess a structure far more complex than that of softwoods. All this complexity arises from the diversity of wood cells (Figure 2. 3), existent in hardwood, with a wide variety of functions, comparatively to softwood. Hardwood cells tissue consist mainly on libriform cells, (support function), vessels (transport function) and ray cells (storage function). It is also possible to find longitudinal tracheids (support function). [4,5,7,8]

Libriform cells are long, with a quite thick cell wall, with small cavities with pits, while vessels are not quite long cells, and exhibit a large width and thin cell wall, with opened or perforated extremities. This last are found linked one after the other, forming channels able to transport water in a more efficient way than tracheids on softwoods. Vessels may exhibit length between 0.3mm and 0.6mm, and width between 30 and 300μm. Its dimension may vary depending on the hardwood species. [4,7,8]

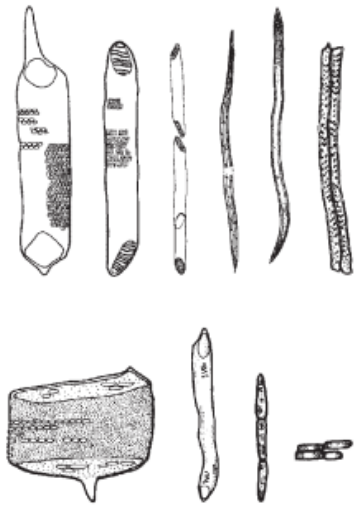

Figure 2. 3- Typical hardwood cells (upper row left to right: aspen earlywood vessel; birch earlywood vessel; birch vessels united, birch libriform fibre; birch tracheid; oak tracheid. Lower row left to right: oak early and latewood vessels, oak longitudinal parenchyma cells, birch ray parenchyma cell) (adapted from [8]).

2.1.3. Wood cell structure

In wood cells, the cell wall is composed by several layers with distinct composition and organization. The thickness and percentage of each component may vary significantly according to cell type, origin, type of wood, etc. [4,8,9]

Cell wall is divided into different layers, the middle lamella (ML), primary wall (P) and the secondary wall, which is formed by the outer (S_1), middle (S_2) and inner (S_3) layers (Figure 2. 4).[4,5,8] Each layer is composed by a cellulose microfibril carcase, which is arranged around the cell in different directions (Figure 2. 4) The microfibril orientation differs from layer to layer being close to 90º in S_1 and S_3 and 10-20º in S_2. In the primary wall microfibrils are not oriented.[5,8]

Wood cells are glued together by means of the middle lamella, being this layer primal function cell adhesion. In its earliest stages it is mainly composed of peptides, evolving then into a highly lignified structure. The lignin content in this layer is the highest being 90-100%. [5,8]

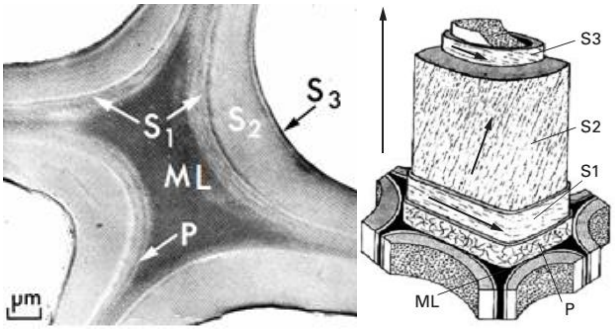

Figure 2. 4- Wood cell wall layers and its orientation, where ML is the middle lamella, P is the primary cell wall, S_1 is the secondary cell wall exterior layer; S_2 is the secondary cell wall middle layer and S_3 is the secondary wall inner layer. [5,8]

The primary wall is the outer layer of cell wall, and consists on a thin layer, whose composition includes, mainly, cellulose, hemicelluloses, pectin and proteins, under a lignin matrix. On its most external part cellulose microfibrils are organized randomly, while in the interior they are orientated nearly perpendicularly to the cell axis.[5,8]

The secondary wall, as mention before, can be divided into three layers, one thinner and more exterior, S_1; an interior layer, S_3 and a middle layer, S_2 (Figure 2. 4). All layers are composed of microfibrils, embedded in a matrix of lignin and hemicelluloses.[8] The outer layer, S_1, is rather thin (0.2-0.3μm thick). Here microfibrils orientation is almost horizontal, with respect to cell axis, while in S_2 it takes almost vertical orientation, followed once more by horizontal orientation, on S_3.[5,8] All these layers, have distinct composition, composed essentially by cellulose in a matrix of hemicelluloses and lignin.[4,5,8]

2.1.4. Wood composition

The chemical composition of wood cells varies significantly depending on the species. The amount of each compound may differ according with various factors such as, the tree age, the type of wood, the part of the tree (leaf, stem, root), geographic localization, climate, soil, etc. Nevertheless, overall, wood is best described as a composite made of cellulose networks, glued with lignin and hemicellulose, with minor amounts of extractives and inorganics.[9,10]

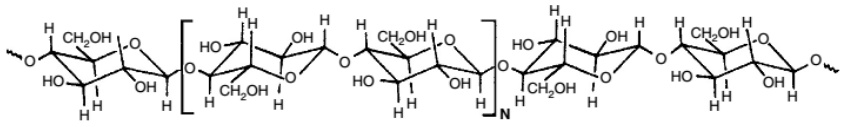

Figure 2. 5 – Cellulose partial structure. [9]

Cellulose is the main constituent of wood, and it consists on a linear polymer made of β-D-glucopyranose units (Figure 2. 5). Its polymerization degree may go up to 10 000. On the other hand, hemicelluloses, are a group of lower weight polymers, made of different sugars units, such as D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid and other less abundant sugars such as L-rhamnose or D-fucose (Figure 2. 6). [9]

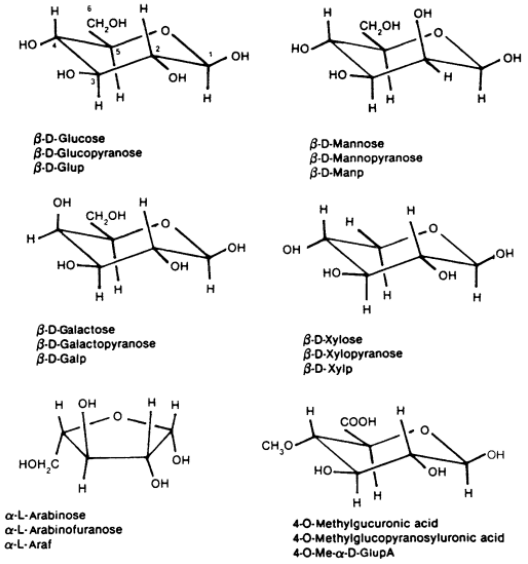

Figure 2. 6 - Sugar monomers from wood hemicellulose (the designations D (dextrogyre) and L (levogyre) refers to the standard configurations for the two optical isomers of glyceraldehyde, the simplest carbohydrate, and designate the conformation of the OH group at carbon 4 (C-4) for pentoses (xylose and arabinose) and C-5 for hexoses (glucose, galactose, and mannose). Also, greek letters α and β refer to the configuration of OH group on C-1. The two configurations are called anomers.) (adapted from [9]).

There are several groups of hemicelluloses found in wood. Their constitution may include one or more types of sugars, and their designation is often formulated in agreement with their predominant sugar monomers, for example, galactoglucomanans, arabinoglucuronoxylans, glucomanans, glucoronoxylans, etc (Figure 2. 7). [3,9,11]

In hardwood, 4-*O*-methyl-glucuronoxylans, known as glucuronoxylans or xylans, are a class of predominant hemicelluloses on this type of wood (ca. 15-30% on wood). Its backbone is constituted by β-D-xylose linked by β(1-4) bonds, with acetyl groups at C-2 or C-3 of the xylose units on an average of 5-7 acetyls per ten xylose units. This polymer is also substituted with sidechains of 4-*O*-methylglucuronic acid units linked to the hemicellulose backbone by α(1-2) links with an average frequency of approximately one uronic acid group per ten xylose units. [9–11] Besides xylans, in hardwood, it is also possible to find glucomanans, (approximately 2-5%), which comprises a polymer constituted by D-glucose and D-mannose units, with an approximate ratio of 1:1 to 1:2. [4,8]

In softwoods galactoglucomanans are predominant hemicelluloses, accounting for approximately, 20%. This polymer may be linear or slightly branched, and its backbone is constituted of D-glucose and D-mannose units, linked by β(1-4) bonds with a molar ratio of 1:2 to 1:3, with branches containing galactose linked to the main backbone by α(1-6) bonds.[10,11]

Xylans from softwood are arabinoglucuronoxylans. This polymer backbone consists of D-xylose units linked by β(1-4) links and branched with 4-*O*-methyl–α-D-

glucopyranosyl uronic acid (linked by β(1-2) links to the backbone) and branched with terminal L-arabinofuranose (linked through α(1-3)links). [9,11]

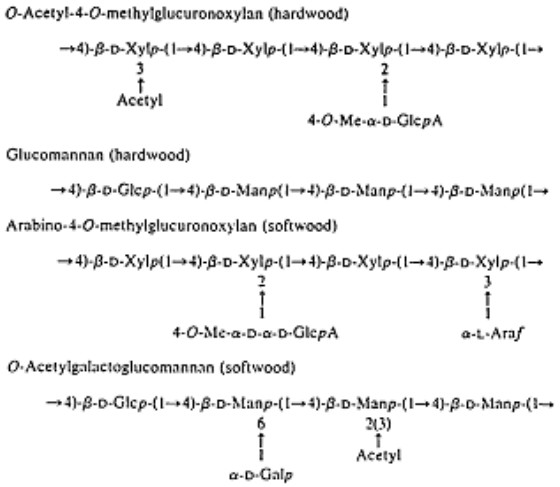

Figure 2. 7 – Structures of hemicelluloses commonly found on hardwood and softwood (adapted from [10]).

Besides hemicelluloses, lignin is another major component of wood. It consists of a branched, amorphous polymer, obtained by radical polymerization of coniferyl, sinapyl and *p*-cumaryl alcohols (Figure 2. 8), where all phenylpropane units are linked by ether and carbon-carbon links. The most abundant bonds in lignin are β-*O*-4 (40-60%), β-5'(5-10%), β-β'(5-15%), 5-5'(5-15%) and 4-*O*-5' (2-8%).[12,13]

Lignin is distributed through all wood tissues, however, as previously mentioned, its concentration is the highest in the middle lamella. It plays a role as a glue in the cell wall containing cellulose fibrils.[8,14]

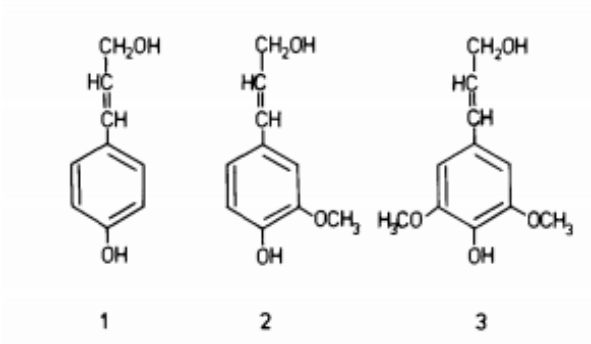

Figure 2. 8- Lignin precursors *p*-comaryl alcohol (1), coniferyl alcohol (2) and sinapyl alcohol (3).[12]

Wood also contains small amounts of extractives, which consist mainly of fatty acids, resins, esters, wax, fats, polyphenolics and terpenes.[3,9,15] The general chemical composition of some wood and non-wood plants is presented in Table 2. 1.[2]

Table 2. 1– Chemical composition of different cellulosic materials. (adapted from [2,16]).

Raw-material	Composition (%)				
	Cellulose	Hemicellulose	Lignin	Extractives	Ash
Hardwood	43-47	25-35	16-24	2-8	0.2-0.5
Softwood	40-44	25-29	25-31	1-5	0.1-0.3
Kenaf	36	21	18	2	2.0-2.5
Sisal	73	14	11	2	1.5-2.0
Cotton	95	2	1	0.4	1.0-4.0

2.1.5. Cellulose

Cellulose is a linear natural homopolymer composed of D-anhydroglucopyranose units (AGU), which are linked together by β(1-4) glycosidic linkages. Its linear structure is attributed to the type of linkages established between each AGU unit. The glucose residues are linked 180° towards each other, making the repeated unit a cellobiose residue (dimer) rather than a glucose residue (Figure 2. 5). [11,17–19]

2.1.5.1. Supramolecular structure

Being a linear polymer with multiple OH groups, cellulose chains exhibit a high tendency to interact with each other (by hydrogen bonds) forming molecule bundles. The formation of a cellulose bundle is often referred to as elementary fibrils. This group of molecules, may be further divided into regions of higher or lower organization, crystalline and amorphous regions, respectively. Elementary fibril may also form aggregates, named microfibrils, which may also do the same, yielding macrofibrils (Figure 2. 9 and 2.11Figure 2. 10). [8,19,20]

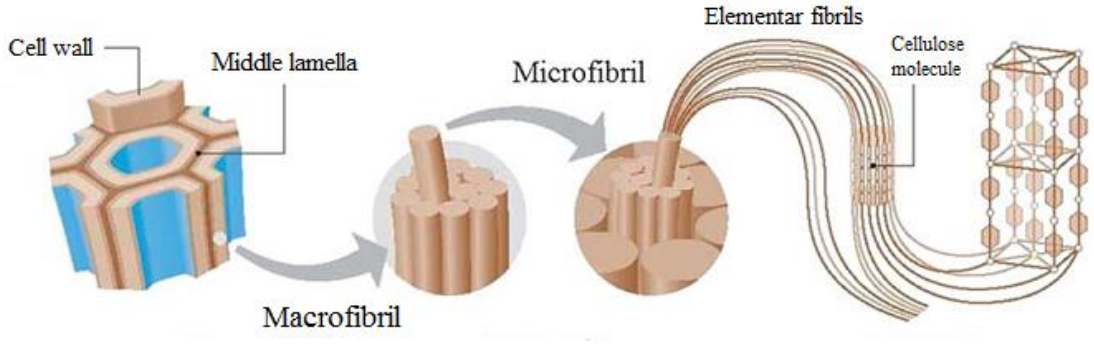

Figure 2. 9 - Scheme illustrating the arrangement of cellulose units in the plant cell wall (adapted from [21]).

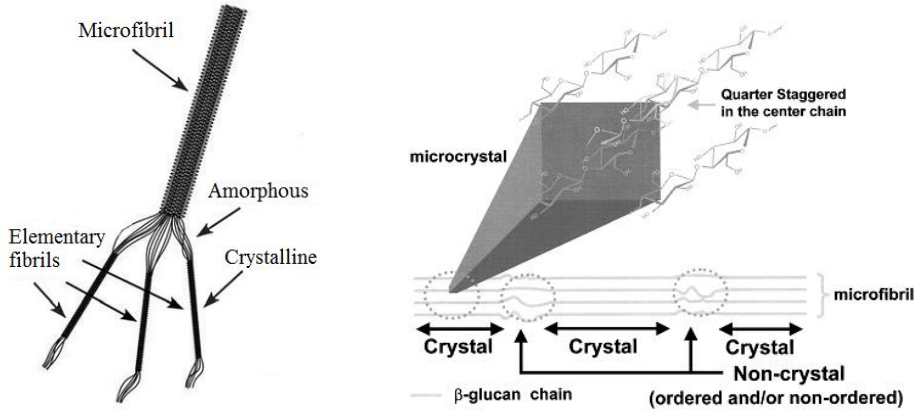

Figure 2. 10- Amorphous and crystalline regions in elementary fibrils (adapted from [22] and [23]).

The surface of cellulose chains contain free OH groups, which are not only responsible for cellulose supramolecular structure but also for its chemical and physical properties. Hydroxyl groups interact with one another by hydrogen bonds, which comprises most of cellulose supramolecular structure. In cellulose two types of hydrogen bonds may be distinguished, intramolecular bonds (bonds between OH groups of adjacent AGU units in the same cellulose molecule) and intermolecular bonds (bonds between OH groups of adjacent cellulose molecules). While the first ones confer a certain stiffness to single chains, the second ones are responsible for the formation of cellulose supramolecular structure. [20,23,24]

Infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, and x-ray diffraction (XRD) studies have enabled the identification of cellulose interactions and organization. [25] It has been demonstrated that cellulose establishes intramolecular bonds OH-3…O5' and OH-2…O6', which confer rigidity to the four ring layer configuration. Intermolecular hydrogen bonds OH-6…O3, also play a key role, since they bond cellulose layers laterally. [11,19,23,26,27] In Figure 2. 11 it possible to observe both inter and intramolecular bonds established by cellulose.

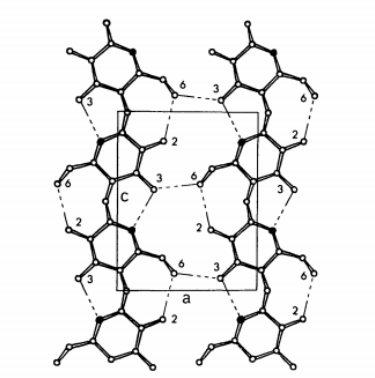

Figure 2. 11- Scheme illustrating the bondings between cellulose molecules (adapted from [9]).

As the packing density of cellulose increases, crystalline regions are formed. The presence of crystalline regions on cellulosic materials brands it as paracrystalline and its percentage of crystalline material is usually around 60-70%. [9,19]

It is possible to find cellulose with different packing/conformations, and therefore with different unit cell parameters. The unit cell is the basis building block of a crystal, repeated infinitely in three dimensions. It is characterized by three vectors a, b and c and the angles between the vectors, α the angle between *b* and *c*; β, the angle between *a* and *c*; and γ, the angle between *a* and *b*.[28]

Cellulose ability of exhibiting different conformations is a case of polymorphism, which in crystallography refers to the existence of more than one crystalline conformation. Cellulose has many polymorphs (cellulose I, II, III and IV), however cellulose I is the native predominant crystalline form of cellulose.[19,28,29]

Cellulose I or native cellulose molecules are organized on a monoclinic unit cell, with two parallel running chains and with cell parameters a=8.35Å, b=10.3Å, c=7.9Å and γ=96-97º (Figure 2. 11). [17,19,26]

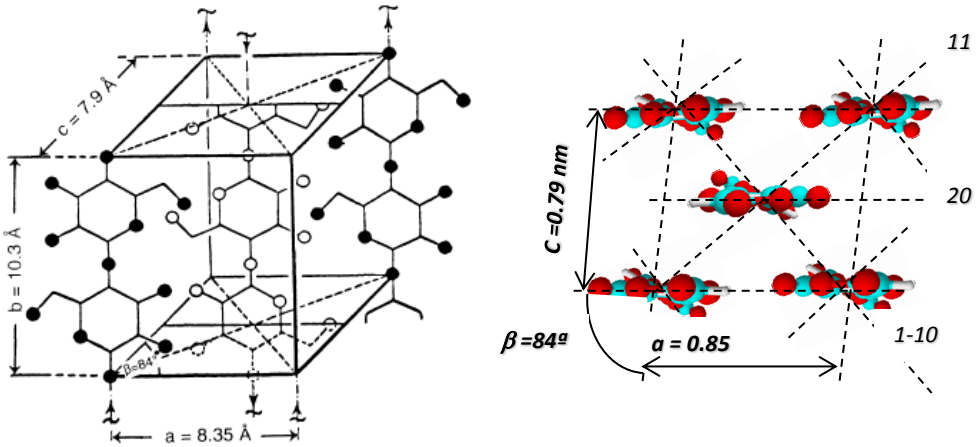

Figure 2. 12 - Scheme illustrating cellulose monoclinic cell structure and its lattice planes (adapted from [19]).

As mentioned above, cellulose has many polymorphs, which exhibit different cellulose packing/organization. The type of conformation and packing displayed by cellulose chains differs from each polymorph and it may be accessed through the aforementioned methods (XRD, IR and NMR). Small variations on the unit cell may be found for the same polymorph depending on cellulose origin.[17,19,28]

Cellulose I is the native and predominate crystalline structure, although it can be converted into the other polymorphs through a variety of treatments. Nevertheless, two forms of cellulose I exist, cellulose I_α and cellulose I_β. Cellulose I_α appears dominantly in bacterial and algal celluloses and contains triclinic cell structure, while cellulose I_β is

predominant in higher plants such as cotton and wood and contains monoclinic cells structure.[19,27,29]

Cellulose I conformation may be altered, irreversibly, into other stable crystalline form, cellulose II. This process may be conducted by two distinct methods regeneration and mercerization. Regeneration process consists in the dissolution of cellulose with an appropriate solvent followed by its recrystallization. As for mercerization it is performed by inciting cellulose intracrystalline swelling with NaOH concentrated solutions, followed by its washing and recrystallization. The fact that the transition from cellulose I into cellulose II is irreversible, implies that cellulose II is a more stable form, with respect to cellulose I. [19,27,29]

Other cellulose polymorphs may be prepared from cellulose I. Such is the case of cellulose III, which is obtained by treatment of cellulose I with liquid ammonia or certain amines (e.g. ethylene diamine, EDA). Cellulose III may also be prepared from cellulose II. The difference on the starting material (cellulose I or II) either renders cellulose III_I or cellulose III_{II}, respectively. Additionally, by treating cellulose III with high temperature and glycerol it is possible to achieve cellulose IV polymorph. Hence, once more, two types may be attained, either cellulose IV_I or IV_{II}, respectively, obtained from cellulose III_I and III_{II}. [19,27,29]

2.1.6. Cellulose accessibility and its interaction with water

In crystalline regions the interactions between cellulose chains are very strong, which explains the high resistance of cellulosic fibres and its insolubility towards most solvents. On the other hand, in its amorphous regions, the higher spacing between cellulosic chains and reduced organization enables a higher availability of free OH groups for interaction with other molecules, such as water. The fact that cellulose has its hydrophilic groups available, makes it highly hygroscopic, with high water absorption capacity.[9,30]

As previously referred, cellulose in wood may be crystalline and amorphous and thus inaccessible and accessible. Accessibility refers to the availability of cellulose functional groups to water, chemicals, microorganisms, etc. Even though crystalline cellulose is inaccessible, its surface is accessible. Moreover, most of amorphous cellulose is accessible but is also covered with hemicelluloses and lignin, which affects negatively its accessibility. [9,19,30,31]

Cellulose accessibility has been investigated by many researchers considering different techniques, such as X-ray diffraction, absorption of infrared radiation, or even

exchange of hydroxyl hydrogen for deuterium or tritium.[9,19,30–34] However, only moisture sorption isotherms will be further discussed in detail.

2.1.6.1. Moisture sorption

As mentioned above accessibility may be evaluated considering sorption experiments with inert gases (N_2 or Ar) or with water vapour. In case of water, this last is able to interact with cellulose, by disrupting weaker hydrogen bond, not being able, however, to interfere with intern crystalline regions. The moisture uptake at certain conditions (temperature and relative humidity) is a rather relevant criteria when evaluating cellulosic fibres interaction with water. [19,35]

The determination of water vapour or moisture sorption isotherms is often used not only to evaluate materials accessibility, but also to analyse materials hydration. This information becomes crucial regarding the papermaking applications, when the hydration abilities of cellulosic fibres predetermines the fibres properties. [19,36] The composition of a cellulosic pulp, the presence of oxidised functional groups, fibres porosity, its surface area and its hydrophilicity/hydrophobicity are rather relevant factors, which may influence moisture sorption. Therefore, this method works as an indirect tool to evaluate the accessibility of free OH groups in fibres. [37]

Moisture sorption isotherm may be determined by means of three different measuring techniques: gravimetric, manometric or hygrometric methods. In the gravimetric method, the weight of the sample is measured using a scale, while in the manometric method, the vapour pressure of water is measured when it is in equilibrium with a sample at given moisture content. In the hygrometric methods, the equilibrium relative humidity with a sample at a given moisture content is measured.[38]

Moisture sorption isotherms can be achieved from completely dried samples, under an environment with controlled humidity, until equilibria is reached. The data is afterwards represented as moisture uptake at equilibrium (X_{eq}), as a function of water activity (a_w), or relative humidity ($RH\%$). In Equation 2.1 it is possible to observe the relationship between a_w and $RH\%$. [37,38]

$$a_w = \frac{RH\%}{100} \qquad \text{Equation 2. 1}$$

Materials water sorption is a process where water molecules progressively and reversibly combine with a material by chemisorption, physical adsorption, and multilayer condensation. An isotherm may assume the shape represented in Figure 2. 13 and it may be divided into three main regions. Region *A* represents strongly bound water (which includes structural water and monolayer water), whose enthalpy of vaporization is higher than that

of pure water. Theoretically, in this layer the moisture content comprises the first layer of water molecules, which are sorbed by hydrophilic and polar groups of materials. These water molecules are unfreezable and hence not available for reaction or as plasticizers (the different types of water in cellulose will be further discussed later on **2.1.6.2.**).[19,37,38]

Region *B* represents the multilayer region, where water molecules are fairly strongly bound, on multiple layers but, not in direct contact with the adsorbent surface.[39] Bonds are less intense, yet with an enthalpy of vaporization still higher than that of pure water. This region can be seen as a transition region from bound to free water. Here water molecules properties are closer to those of free water, and are available as solvent for low-molecular weight solutes and for some biochemical reactions. Also, water molecules from this region usually do not freeze at normal freezing point.[37,38]

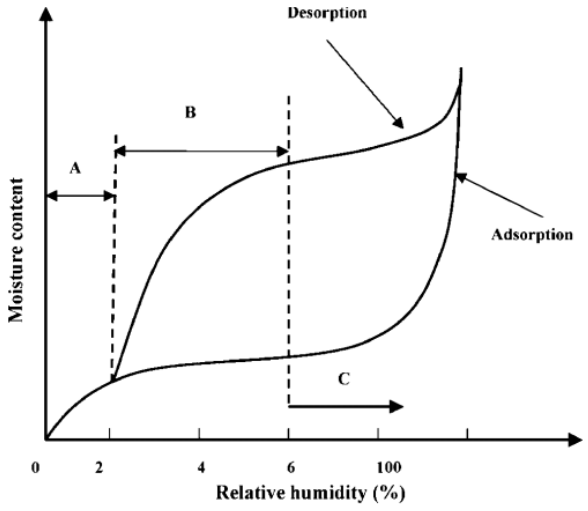

Figure 2. 13 - Representation of a moisture sorption isotherm and the hysteresis phenomena associated with it (adapted from [38]).

In region *C* it is represented the region of capillary condensation, where the sorbed water is not bound by surface forces and is free to condense as liquid phase, within the molecular capillaries. The properties of water molecules start approaching those of bulk water. [37–39]

Between sorption and desorption (Figure 2. 13) the occurrence of hysteresis may be related with the nature and state of the components of materials, reflecting their potential for structural and conformational rearrangements, which alters the accessibility of energetically favourable polar sites. [35,37]

Moisture sorption isotherms may be classified according with *Brunauer et al.*[40] and therefore be divided into five types (I, II, III, IV and V). [40,41] Type I isotherms, often referred to as Langmuir isotherms (monolayer coverage), are concave to a_w axis and approach a limiting value as $a_w \rightarrow 1$. This isotherm is typical on microporous materials. [40–

[42] Type II isotherms are the usual on non-porous or macroporous adsorbents. Thus represent unrestricted monolayer-multilayer adsorption. The border between region A and B, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption is about to begin. It is typical on hydrophilic materials, such as cellulose, and is indicative if strong adsorbate-adsorbent interactions.[41–43] Type III isotherms are convex to a_w axis over its entire range and therefore do not exhibit monolayer. This type of isotherm suggests a hydrophobic surface, reluctant to accept water. It shows weak interaction between adsorbate and surface.[41–43] Type IV isotherm are typical on mesoporous materials. The initial part of this isotherm is attributed to monolayer-multilayer adsorption, since it follows the same path as the corresponding part of a type II isotherm, but at higher a_w the isotherm tends to a plateau. It reflects capillary condensation which result in effective reduction of available surface for further adsorption.[41,42,44] Type V isotherms are uncommon and related with type III, with weak adsorbent-adsorbate interaction. They occur in porous adsorbents (either meso or microporous), such as the case of highly porous hydrophobic carbon materials with water vapour. Similarly to type IV, it represents mono and multilayer adsorption plus capillary condensation. [41,42,44]

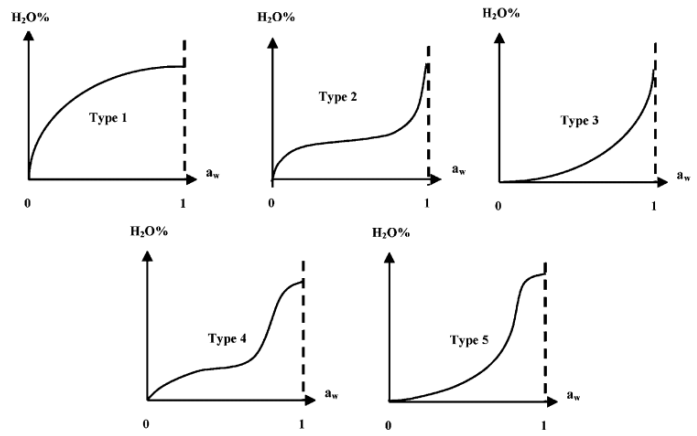

Figure 2. 14 – Types of isotherms according with *Brunauer et al*.(adapted from[38]).

Moisture sorption isotherms can be described by mathematical models, which are able to fit moisture sorption isotherms data in different environmental conditions. Many model equations have been developed and the approaches vary from empirical curve fitting to models based on various degrees of understanding of the mechanisms involved.[36] However, no model can be considered completely accurate, since for different water activities, different mechanisms of water molecules association may occur.[36,37,45]

Numerous models can be found on literature, and these may be discriminated according with its main fundamentals (Table 2. 2), such as, models based on monolayer

(e.g. BET model), models based on multilayer (e.g. GAB model), semi-empirical models (Henderson and Halsey model) and empirical models (e.g. Oswin model). [36,37,45]

Table 2. 2 – Examples of some moisture sorption isotherm models.[37,38,45]

Model	Equation	Observations
BET (*Brunauer, Emmett e Teller*)	$X_{eq} = \frac{X_m C a_w}{(1-a_w)(1-a_w+Ca_w)}$	-Langmuir mechanism; -Monolayer; - 0,05<aw<0,5;
GAB (*Guggenhein-Anderson-de Boer*)	$X_{eq} = \frac{X_m C K a_w}{(1-Ka_w)(1-Ka_w+CKa_w)}$	- Monolayer formation, followed by multilayer formation; -usually applied between 0.1<aw<0,9
Halsey	$a_w = exp\left(\frac{-A}{\theta^r}\right)$	-Semi-empirical - 0.1<aw<0,9 - Molecules potential energy varies with the potency of the distance to the surface; -Sigmoidal
Henderson	$X_{eq} = \left[\frac{\ln(1-a_w)}{-A}\right]^{1/B}$	- Semi-empirical - Sigmoidal
PELEG	$X_{eq} = k_1 {a_w}^{n_1} + k_2 {a_w}^{n_2}$	- Semi-empirical - Sigmoidal or not; -very versatile; -Good for polymers such as starch
Oswin	$X_{eq} = A\left[\frac{a_w}{1-a_w}\right]^B$	- Empirical - Sigmoidal -0.1<aw<0,9;
Smith	$X_{eq} = A + Blog(1-a_w)$	-Empirical - Biological materials such as starch - 0.1<aw<0,9;

In case of cellulosic materials BET and GAB models, especially GAB, have demonstrated rather good ability to fit and describe moisture sorption data on different cellulosic materials. [36,46]

Brunauer-Emmett-Teller (BET) model [47], was proposed in 1938, and is widely used in food science. Its versatility allows to describe moisture sorption on different materials. It is typically used to describe type II and III isotherms, and from it, it is possible to estimate the monolayer coverage. However, only at water activities inferior to 0.45. [42,48] Its principles are based on the following hypothesis, (i) the rate of condensation on the first layer is equal to the rate of evaporation from the second layer, (ii) the binding energy of all of the adsorbate on the first layer is the same, and (ii) the binding energy of the other layers is equal to that of pure adsorbate.[36,42,45]

BET equation is represented in Table 2. 2, where X_{eq} is the moisture uptake at equilibrium, X_m is the monolayer moisture content, a_w the water activity, and C a constant.

Guggenheim, Anderson and de Boer isotherm model (GAB), is also a well-known and quite versatile model, not only widely used on food science, but also for cellulosic materials. It is considered to be a refinement of Langmuir and BET theories, with three parameters, with physical meaning. [36,42,45,49]

In Table 2. 2 is represented GAB model equation, which is much similar to that of BET. Similarly to BET, X_{eq} is the moisture uptake at equilibrium, X_m is the monolayer moisture content, a_w the water activity, and C and k are constants. When k=1, GAB model turns into BET model. [36,42,45,49]

From parameter X_{eq}, it is also possible to estimate the sorbent's specific surface area (S, m^2/g_{solid}) as displayed by Equation 2.2, where M_w is the adsorbate molecular weight, N_a the Avogadro number, and A_m is the effective cross-sectional area of the adsorbate molecule (0.125nm^2 for water at 298 K). [50]

$$S = X_m \left[\frac{N_A A_m}{M_w}\right] \qquad \text{Equation 2. 2}$$

As mentioned previously, GAB parameters have a physical interpretation. Parameter C represents a dimensionless parameter related with the heat of sorption of monolayer, i.e. it is a way of accessing the strength of binding between water and primary binding sites. Higher values of C, suggest stronger interactions between water molecules from the monolayer and the sorbent surface.[37,42,49]

Parameter k, it is also a dimensionless parameter, but now related with the heat of sorption of the multilayer. When k approaches 1, there is almost no distinction between multilayer molecules and liquid ones. Under this circumstance water molecules past the monolayer are not organized in multilayer, however, exhibit similar features of those from liquid water. On the other hand, the more molecules are organized in multilayer, lower is k. The temperature dependence is also considered on GAB parameters C and k, this dependence is shown by Equations 2.3 and 2.4.[37,42,49]

$$\mathrm{C} = \frac{\mathrm{q_1}}{\mathrm{q_m}} = \mathrm{C_0} \cdot \exp\left(\frac{\Delta \mathrm{H_c}}{\mathrm{RT}}\right), \text{with } \Delta \mathrm{H_c} = \mathrm{H_m} - \mathrm{H_q} \qquad \text{Equation 2. 3}$$

$$\mathrm{k} = \frac{\mathrm{q_l}}{\mathrm{q_m}} = \mathrm{k_0} \cdot \exp\left(\frac{\Delta \mathrm{H_k}}{\mathrm{RT}}\right), \text{with } \Delta \mathrm{H_k} = \mathrm{H_l} - \mathrm{H_q} \qquad \text{Equation 2. 4}$$

Here C_0 and k_0 are constants of entropic nature. The first is defined as the accommodation function between the first layer and multilayer, while the second represents the accommodation function between bulk water and multilayer. Usually C_0 exhibits values smaller than 1, due to molecules preference for the multilayer, while k_0 values are expected to be higher than 1, due to the high entropy of molecules in liquid.[37,42,49]

Parameters ΔH_c and ΔH_k represent the difference in enthalpy between monolayer (H_1) and multilayer (H_q), and the difference in enthalpy between bulk water (H_l) and multilayer (H_q), respectively. The first is usually positive, given the exothermic nature of water and primary site for sorption, while the other is often negative and smaller, since the multilayer molecules are bound more loosely. Nevertheless, positive values are possible and have been observed in some foods as the result of endothermic dissolution of fruit sugars. [37,49]

The heat involved in the sorption of moisture can also be estimated. The net isosteric heat of sorption (ΔH_s) evaluates the binding energy existing between the water molecules (vapour state) and the sorbent. It is derived according to the *Clausiys-Clayperon* equation (Equation 2.5) for constant moisture. From this parameter it is also possible to determine total heat of sorption, Q_s, by adding the heat of water vaporization (ΔH_v), (Equation 2.6). [37,49]

$$\Delta H_s = -\mathrm{R}\left(\frac{\partial \ln a_w}{\partial T^{-1}}\right)_{X_{eq}} \qquad \text{Equation 2. 5}$$

$$Q_s = \Delta H_s + \Delta H_v \qquad \text{Equation 2. 6}$$

Parameters ΔH_c and ΔH_k determined from Equations 2.3 and 2.4, also allow a theoretical estimate of the net isosteric heat of sorption, which is given by the relationship displayed on Equation 2.7.

$$\Delta H_{s,t} = \Delta H_c + (-\Delta H_k) \qquad \text{Equation 2. 7}$$

2.1.6.1.1. States of water

Water may be found associated with different materials differently, namely, either on in its free or bound form.[35,51] Bound water exhibits different properties, relatively to that of free water. It is noteworthy the reduced mobility of the first relatively to the second, due to its bound situation. As concerns cellulose, water molecules mobility is restrained by the presence of cellulose OH groups, with which they interact. Some features of this kind of water include lower vapour pressure, superior bounding energy, reduced mobility, inability to freeze at low temperatures and unavailability to act as solvent.[35,51]

Bound water may by further subcategorized into nonfreezing bound water and freezing bound water. Nonfreezing bound water consists on water molecules that are not detected during DSC (differential scanning calorimetry) and may be determined by the difference between the total water measured gravimetrically and the amount of water detected by DSC analysis. When considering water sorption at the fibres surface, it is possible that the first, up to the three first layers of water bound to cellulosic fibres surface,

are not able to freeze. This inability is related with the limitations under water molecules motion imposed by the interactions with cellulosic fibres surface. [35,51,52]

As regards freezing bound water, contrarily to the previous case, a phase-transition is observed, but at temperatures lower than that of bulk water. Since, the strength of the hydration interaction decreases with the distance from the material surface, so water molecules associated with the surface may be frozen at lower temperatures. Studies to access materials states of water may be carried out through methods such as DSC or NMR. [35,51,52]

2.2. Paper feedstocks

In pulp and paper industry the feedstock used may vary greatly. It mainly consists on fibrous raw material which may include primary or secondary fibres. Being primary fibres obtained directly from plant raw materials (mainly from wood or other non-wood plants) and secondary fibres being produced from recovered paper.[53] Considering the feedstocks used for each type of fibres production, these will be divided respectively into virgin fibres and recycled fibres.

2.2.1. Virgin pulps

Wood is the main raw material used to produce cellulosic pulp. Pulping processes are used to produce cellulosic pulp, and its main purpose consists on liberating cellulosic fibres from the wood matrix. In principal, this can be achieved by mechanical, chemi-mechanical, semi-chemical and chemical pulping processes. Additionally, depending on pulps end-use, a bleaching process may follow the pulping process, in order to improve its brightness. [54–57]

2.2.1.1. Mechanical and chemi-mechanical pulps

Mechanical pulping is the original form of pulping. It separates fibres from each other by using only mechanical attrition to wood, with no chemicals (other than water or steam).[56–59] The aim of mechanical pulping resides in maintaining the main part of lignin (and other wood components) to achieve high yield pulp, with satisfactory strength and brightness properties. Mechanical pulping processes exhibit pulp yields of about 90-98%, depending on what mechanical pulping method is being used. However, it usually requires high amount of energy when compared to chemical pulping. [54,57,58]

Mechanical pulps are featured as high yield (high wood components content), high bulk, high stiffness, and low cost pulps. Their low strength is associated with lignin

interference with interfibre bonding. The presence of high lignin content may also cause pulp to turn yellow upon light or air exposure. [57,58]

Furthermore, apart from fibres, mechanical pulp is also known to display a considerate content of smaller structures named fines (pieces from fibres wall and broken fibres), which are responsible for mechanical pulps optical properties. [54,56–58]

The main processes applied for mechanical pulp production include stone groundwood pulping (SGW), pressure groundwood pulping (PGW), refiner mechanical pulping (RMP), thermo-mechanical pulping (TMP), or chemi-thermo-mechanical pulping (CTMP). [56,57][55]

Groundwood mechanical pulp is produced by grinding wood logs, with grindstones on the tangential and radial surfaces (SGW). It may also be prepared by pressurizing the grinder with steam at temperatures of 105-125°C. In this case wood is heated and softened before the grinding process, to improve the separation of fibres with less fibres cutting and less fines generation (PGW). Another example of mechanical pulping is the refiner pulping process (RMP), here pulp is produced by disintegration of chips that are fed to two refining discs, at atmospheric pressure conditions. [54,57][55]

Modifications on mechanical pulping methods may also be performed to produce pulp with a higher amount of long fibres. In these processes lignin may be softened by increasing process temperature. In this case wood chips are pre-treated with steam (approximately 120ºC), before entering the refiners (TMP). It is also possible to combine chemical treatments with mechanical pulping. In that case, wood chips are embedded with sodium sulfite solution to sulfonate lignin and to soften its structure, hence turning easier fibres separation (CTMP).[54,55,57]

Depending on the applications, it is also possible to brighten mechanical pulps with, for example, hydrogen peroxide and/or sodium sulfite. These chemicals only brighten the pulp and do not permanently bleach it.[58]

The use of mechanical pulps is confined mainly to non-permanent papers like newsprint and catalogue paper. Mechanical pulps constitute 20-25% of the world production and this is increasing due to the high yield of the process and increasing competition for fibre resources. [57]

2.2.1.2. Chemical pulp

Besides mechanical pulping, cellulosic pulp may also be produced by chemical pulping. In this process the main purpose consists on solubilizing and remove lignin from wood, so that very little mechanical treatment is required to separate wood fibres from

each other. There is a wide variety of chemical pulping methods and each has its own specific advantages and disadvantages. The most common pulping processes known include the soda pulping, *kraft* pulping and sulfite pulping, although the *kraft* process accounts for the major part of chemical pulps produced all over the word. [54,55,57]

Comparatively to previous mechanical pulping methods, pulps produced by chemical pulping are more flexible, conform better to each other when forming paper and render good strength properties. The cooking procedures may either be continuous or batch-wise. [54,55]

Contrarily to mechanical pulping (high yield pulps) in chemical pulping, only approximately half of the wood becomes pulp, while the other part is removed. In this process, however, little electric energy is required for the process, since most of it is recovered along with most of the cooking chemicals, thanks to efficient recovery systems.[54]

The produced pulp is coloured, and its degree of colouring varies with the pulping process. To produce certain paper grades that require high brightness pulp is bleached.[54] As regards the most commonly used chemical pulping processes these will be briefly scrutinized below.

i) Soda pulping

Soda pulping was one of the first chemical pulping methods invented and it uses sodium hydroxide for the chemical cooking process. After *kraft* process was discovered most soda mills were converted to the *kraft* process. The soda process still has limited use for easily pulped materials such as agriculture residues (e.g. straws) and some hardwoods, but it has lost most of its importance. Soda pulping of woods is possible while using anthraquinones as catalyst.[57]

ii) Kraft pulping

Kraft cooking is the dominant chemical pulping method. In this process the cooking liquor consists of a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), where OH^- and HS^- are the cooking active species. Here, whereas the last plays a key role on delignification, the other keeps lignin fragments in solutions. As previously mentioned, sodium hydroxide alone (soda process) was initially used as the alkaline pulping agent, however, with time, mills were then converted to the *kraft* process due to its ability to produce superior pulp. [54,55,57]

The cooking procedure can either be continuous or batch-wise. In a typical "cooking" process, wood chips are first pre-steamed to turn wood chips "softer" and to

force out any entrapped air. Then, they are combined with a highly alkaline solution, the white liquor, which contains sodium hydroxide and sodium sulfide. All these ingredients are blended together in a digester, where they are pressurized and cooked at 160-170ºC, over several hours. During this time, reactants permeate wood chips and dissolve most of its non-fibrous contents. The cooking conditions may vary, depending on the wood type or the desired pulp quality. [55,57,59] When finished the contents from the cooking process (pulp) are discharged from the digester into a *blowtank*. [54,57,59]

Owing to the use of high amounts of chemicals, its recovery and reuse becomes essential, not only due to economical issues, but also due to environmental issues (residues management). Therefore, in this process the inorganic chemicals, resultant from the pulping process, are recovered and regenerated for reuse. Additionally, large amounts of heat energy are generated/produced from the black liquor combustion.[54,55,60] Typically, pulp and its liquor (black liquor), after the "cooking" process, are separated in a washing process. While pulp proceeds into bleaching (in case of bleached pulp production), "black liquor" is sent off to multi-effect evaporators to be concentrated. This process concentrates the dissolved organic matter (lignin and carbohydrate degradation products) leaving it in conditions to be burned in the recovery furnace. [55,60] The remaining NaOH and sodium salts of organic acids are converted to Na_2CO_3. Also during the combustion sodium sulfate is reduced to sodium sulfide by the carbon (Equations 2.8 and 2.9). Usually, sodium sulfate is added as makeup, being then reduced to Na_2S by carbon. [55,60]

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad \text{Equation 2. 8}$$

$$Na_2SO_4 + 4C \leftrightarrow Na_2S + 4CO \qquad \text{Equation 2. 9}$$

Afterwards, the inorganic share on the bottom of the furnace (Na_2CO_3 and Na_2S) is collected and dissolved in water. Then, the mixture, now "green liquor", is sent into the *slaker*, to get in contact with slaked lime and to turn Na_2CO_3 into NaOH (Equation 2.10). Since Na_2S does not react with lime, the mixture of NaOH and Na_2S ("white liquor") can be reused on another pulping process. [54,55,57,60]

$$(Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3) \qquad \text{Equation 2. 10}$$

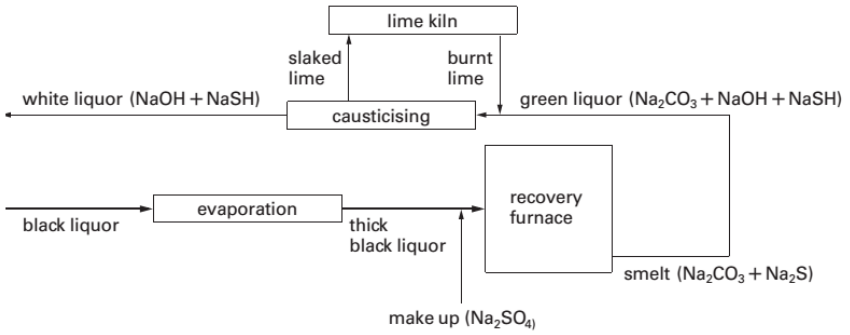

Figure 2. 15 – Scheme of the stages involved on the recovery process of chemicals and energy in the *kraft* process.[54]

The resultant $CaCO_3$ sludge is filtered off, burned in a lime kiln, and reused. Therefore, the chemical system is closed, which minimizes costs and pollution.

Nevertheless, the kraft process still exhibits serious issues as concerns air pollution. These are essentially related with the release into the atmosphere of hydrogen sulfide, mercaptans, and other sulfur compounds, that exhibit a distinct bad odour. Still, the use of various techniques, such as black-liquor oxidation, improved evaporators and furnaces, and control of emissions has been able to mitigate this negative outcome. [54,55,57,60]

The *kraft* process is rather versatile since it may be used in any type of wood pulping process. Additionally, it is able to produce pulps with high strength, with a good energy efficiency and chemicals recovery. Although the disadvantages of this process include difficulties in the bleaching process comparatively to sulfite pulps, low yield (carbohydrate losses) and odour problems related with the emission of sulfur based compounds, that can be detected by the olfactory at 10 parts per billion. Although, as regards this last, it does not appear that this process will be supplanted in the near future; instead, it seems more likely to be improved and modified with time. [54,55,57]

iii) Sulfite pulping

The sulfite pulping process is an example of other chemical pulping process. Here lignin is dissolved by sulfonation with an aqueous solution of sulfur dioxide and calcium, sodium, magnesium, or ammonium bisulfite, cooked at high temperature and pressure in a digester. Today, the dominating base used in sulfite pulping is magnesium.[61] Calcium requires pH 2 to stay in solution, while magnesium allows pH values up to 4. In case of sodium and ammonium sulfite solutions these can be strongly alkaline without precipitation. Acid processes are those in which pH is between 2 and 3, bisulfite processes operate at pH range of 3-5, neutral sulfite processes in the range of pH 6-9, and alkaline sulfite processes are above pH 11. [62]

Regardless of the base used, the initial step of sulfite pulping consists on the preparation of the "cooking" liquor, which is commonly prepared at the mill by burning sulfur to produce SO_2 and dissolving it in water to produce sulfurous acid (H_2SO_3). During combustion of sulfur, it is imperative to regulate the amount of oxygen to guarantee a complete oxidation and avoid over oxidation (formation of SO_3). The SO_2 gas is then rapidly cooled down (to minimize SO_3 formation, that originates sulfuric acid in water), prior to reaction with water. After cooling down, the SO_2 gas must be absorbed in water and react with the proper base to form the cooking liquor. Equation 2.11 to 2.14 represent the referred reactions, where M = Na, K, NH_4, ½ Ca or ½ Mg (in aqueous solution) [55,57,61]

$$S + O_2 \rightarrow SO_2 \quad \text{Equation 2. 11}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad \text{Equation 2. 12}$$

$$H_2SO_3 + MOH \leftrightarrow MHSO_3 + H_2O \quad \text{Equation 2. 13}$$

$$MHSO_3 + MOH \leftrightarrow M_2SO_3 + H_2O \quad \text{Equation 2. 14}$$

In sulfite process, temperature control and uniform distribution of liquor play major roles. Heat is only supplied partially at the beginning, until uniform impregnation of wood chips is achieved. For a uniform impregnation of wood, long times are required. Sulfurous acid tends to penetrated wood chips rather rapidly, relatively to the base, leading to a high concentration of acid on the wood chips. So long times are required to allow bases to buffer the system and avoid wood chips to char. Afterwards temperature is further raised, until reaching a chosen value. At the end the pressure on the digester is reduced (decompression), which causes wood fibres to separate. Process conditions may vary according with wood species, ion base, temperature, pulping time (8-14h), amount of acid and ratio liquor to wood.[55,57,61]

Overall, sulfite pulping exhibits yields between 40-52%, and produces medium strength pulp, with soft, flexible fibres. Lignin content is low, so pulps are easily bleached, being required less chemicals when compared with kraft process. [55,57,61]

There are four basic sulfite pulping processes currently in commercial use, these include acid sulfite, bisulfite, neutral sulfite, and alkaline sulfite processes. Being the main differences between one another the levels of acidity and alkalinity used to break down wood and remove lignin (Table 2. 3). [55,57,61]

Table 2. 3 - Sulfite pulping processes conditions (adapted from [61]).

	Initial pH range at 25ºC	Base alternatives	Active species
Acid sulfite	1-2	Ca^{2+}, Mg^{2+}, Na^+, NH_4^+	H^+, HSO_3^-
Bisulfite	3-5	Mg^{2+}, Na^+, NH_4^+	H^+, HSO_3^-
Neutral Sulfite	6-9	Na^+, NH_4^+	HSO_3^-, SO_3^{2-}
Alkaline Sulfite	10-13.5	Na^+	SO_3^{2-} , OH-

In sulfite processes it is also possible to perform chemical recovery of reactants. Overall, the process consists initially in the washing of the pulp liquor, then on its concentration, burning (heat generation during combustions), chemicals regeneration and by-products recovery. However, burning liquor to recover chemicals does not apply entirely to all chemicals. An example is ammonia that is converted into H_2O and N_2 through the burning process. [55,57,61]

However, bases such as, Mg^{2+} and Na^+ are possible to recover. For example, magnesium is possible to be recovered from burning of the cooking liquor, by recovery of

gases as MgO. This last is posteriorly slurried in water to render Mg $(OH)_2$ and then used to trap SO_2 and generate Mg $(HSO_3)_2$.[57,61]

Sulfite process, oppositely to kraft are unable to cook softwoods such as pine. However, the produced pulps have high alpha-cellulose content ("pure" cellulose content extracted from fibres, stable, with high polymerization degree), which are used to produce, for example, rayon. [57,61]

2.2.1.3. Semi-chemical pulps

In addition to the methods previously described, it is also possible to conjugate both chemical and mechanical treatments to produce cellulosic pulp, semi-chemical pulp. In this case the wood chips are initially treated with a mild chemical treatment and then subjected to mechanical treatment (refining) to separate fibres from one another. In this process lignin and hemicelluloses are partially removed, rendering pulps with yield of 60-80%. The initial chemical treatment principles may be alike to those of chemical pulping (previously discussed), differing in process conditions such as cooking time, chemicals charge, etc. [55,57]

Neutral sulfite semi-chemical, NSSC, is an example of a common semi-chemical pulping method (yields of 75-85%). Here an initial chemical treatment is applied to wood, often including Na_2SO_3 and Na_2CO_3, with a slightly alkaline medium (pH 7-10). Cooking times are short, 0.5-2 h at 160-185°C .[55,57]

Due to the amount of residual lignin in fibres, these exhibit a certain stiffness. Moreover, the cooking liquor deficiency in lignin, hinders the chemicals recovery process. Owing to that, in most cases, semi-chemical mills are integrated with chemical mills to allow the recovery of chemicals (from their cooking liquors), which may be used as make up chemicals on the chemical pulp mill. [55,57]

Although bleachable semi-chemical pulps require large amounts of bleaching chemicals. NSSC pulp is used mostly for the production of corrugating medium.[55,57] Most pulping methods discussed on section **2.1.1.**, used for the production of pulps from wood are summarized in Table 2. 4.

Table 2. 4- Typical pulping processes used in the production of virgin pulps (adapted from [57]).

Process	Chemicals	Species	Pulp Properties	Uses	Yield %
Mechanical pulping	None; grind stones for logs; disk refiners for chips	Hardwoods and some softwoods	High opacity, softness, bulk, low strength and brightness.	Newsprint, Books, magazines	92-96%
Chemi-mechanical pulping	CTMP; mild action; NaOH or $NaHSO_3$		Moderate strength		88-95%
Kraft process, pH 13-14	NaOH + Na_2S; unlined digester, high recovery of pulping chemicals, sulfur odor	All woods	High strength, brown pulps unless bleached	Bags, wrapping, linerboard, bleached pulps for white papers	65-70% for brown papers; 47-50% for bleachable pulp 43-45% after bleaching
Sulfite, acid or bisulfite	H_2SO_3+HSO_3^- with Ca^{2+}, Mg^{2+}, Na^+ or NH^{4+} base; Ca^{2+} is traditional but outdated since no recovery process; lined digesters	Hardwoods	Light brown pulp, if bleached, easily bleached to high brightness, weaker than *kraft* pulp, but higher yield	Fine paper, tissue, glassine, strength reinforcement in newsprint	48-51% for bleachable pulp; 46-48% after bleaching
	Mg^{2+} base	Almost all species	Same as above but lighter colour and slightly stronger	Newsprint, fine papers, etc.	50-51% for bleachable pulp; 48-50% after bleaching;
Neutral sulfite semi-chemical (NSSC) pH 7-10	Na_2SO_3 + Na_2CO_3 about 50% of the chemical recovered as Na_2SO_4	Hardwoods (preferred)	Good stiffness and moldability	Corrugating medium	70-80%

2.2.1.4. Pulp Bleaching

The cellulosic pulps produced by the pulping processes usually exhibits a dark color, namely, a brown tonality. Although this feature does not represent an issue for certain applications, in other cases it represents a rather significant matter. The colour displayed by pulp is mostly attributed to the presence of chromophore substances and residual lignin (compounds able to absorb light and, thus, confer colour). Therefore, to improve pulp brightness, pulp is treated with chemical agents able to degrade and/or remove selectively chromophore structures, while preserving its polysaccharides. However, bleaching also removes hemicellulose and extractives.[55,63–65]

Bleaching processes may occur in two ways, either with the removal of lignin (delignification), or by preservation of lignin and degradation of some chromophore structures. This last is mostly applied to high yield pulps (mechanical pulps), while the other is applied to chemical pulps. [55,63–66]

Various chemicals may be used to improve pulps brightness. In pulp mills, bleaching involves a set of stages which include bleaching and alkaline extraction. Chemicals used on bleaching include chlorine (C), chlorine dioxide (D), sodium hypochlorite (H), oxygen (O), hydrogen peroxide (P), ozone (Z), and more recently enzymes (X). Sodium hydroxide usually functions as extraction reagent (E). [55,63,65,66]

However, due to environmental issues (production of organochloride compounds), it became necessary to abandon certain chemical reagents. Conventional bleaching methods based on chlorine and sodium hypochlorite were replaced by ClO_2 or even by other technologies based on oxygen (O), hydrogen peroxide (P), ozone(Z) and more recently enzymes (X), rendering elemental chlorine-free (ECF) and totally chlorine free (TCF) bleaching processes. [55,63,65,66]

From all the referred agents, the use of enzymes is the newest one. In an enzymatic stage different enzymes may be used. An example would be the employment of xylanase. Its hydrolytic action towards its surrounding hemicelluloses (namely xylans) turns lignin vulnerable to oxidation by hydrolysis.[55,67] The progress in bleaching is followed by measuring brightness, more specifically the reflectance of visible blue light at 457 nm (ISO standard norm)[66]

2.2.2. Recycled pulp

Besides virgin pulp, recycled fibres are also an important source of cellulosic pulp. On nowadays paper industry their presence has grown as replacements of virgin pulps. An example of this would be the increase of paper recycling in Europe in 2011 of 70.4%. This growth, overall may be attributed to various facts such as its cost (virgin fibres became expensive due to its limited availability), along with environmental and ecological concerns. Besides, the constant evolution on the deinking technology has enabled paper recycling processes to became, with time, more efficient and eco-friendly, relatively to those used to produce virgin fibres. [68,69]

As stated before, paper industry is increasing its use of recycled fibres (Figure 2. 16). They are majorly applied on packing products, newsprint and hygiene paper production.[70,71]

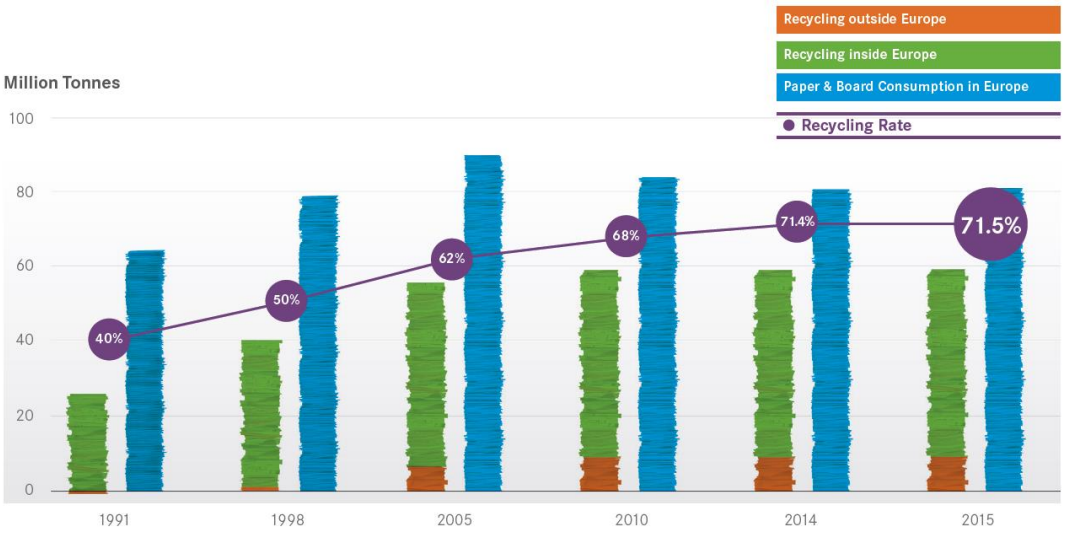

Figure 2. 16 – European Paper Recycling between 1991 and 2015.[72]

2.2.2.1. Deinking

The process of paper recycling passes through deinking. The deinking process consists on a sequence of different treatments, with the main purpose of removing ink and other impurities from fibres. [70,73]

i) Paper waste assembly

It begins with the assembly of paper waste, the raw material used to produce recycled fibres. This process also includes a sorting stage, where paper wastes are sorted into different categories, made into bales, and transported into the paper mill, where paper waste will be converted into recycled pulp. The sources of paper waste consist mostly on Old newsprint (ONP), Old magazines (OMG), mixed office waste (MOW) and other higher grade papers along with old corrugated containers (OCC). The combination of all these operations makes it a rather expensive process. Moreover, the variability of the feedstock meant for recycling, may afflict variations on the deinking process.[68,70,73]

The bales of waste paper received on the paper mill are then subjected to series of process treatments.[70,73,74] Emphasis will be given to key deinking operations, namely pulping, floatation and washing. Even though bleaching is an optional stage aiming to improve recycled paper brightness, this operation will also be discussed.

ii) Pulping and screening

When received, papers wastes are fed to a pulper for disintegration into fibres. During repulping (slushing), waste paper is soaked, disintegrated, and ink and other impurities start to detach from fibres. If the paper waste (fibres source) exhibits rather high wet strength, a disperser may be used to aid fibre separation. Chemicals, temperature or both aid the process. Chemicals, such as sodium hydroxide, sodium silicates and EDTA may be used to improve fibre wetting, disintegration and impurities detachment.[70,73,74]

Other contaminates such as plastic materials, metals and other types of impurities may also be removed on *refuse removal*, *high-density cleaning* and/or *screening stages*.[70,73,74]

Screening is used to remove and minimize the aforementioned impurities as early as possible. In this process the impurity particles are retained by a screen and thus separated from the fibres. For an optimized process screens not only contain rotors and screen hole baskets, but also a cyclone function to separate heavy from light portions.[70,73,74]

iii) Floatation and Washing

The main operations used in deinking consist on flotation and washing, whose main objectives are the removal of ink along with other impurities.

In the case of floatation, the hydrophobic particles made of impurities (whose major component are inks), coalesce into larger particles, aided by chemicals and air bubbles, towards the surface. Then, the formed froth is removed. This process may be influenced by variables such as water hardness, pH, consistency, particle size and temperatures (usually 40-45ºC). To aid the process, chemicals such as calcium soaps are often used. These chemicals are named collectors, since their job consists, mostly, on promoting impurities agglomeration, by enhancing the chemical interaction between its particles and air bubbles. Other chemicals, often used on this process consist on sodium hydroxide, (pH increase, fibre swelling, emulsification), fatty acid soaps (collectors), and surfactants (improve ink detachment). [70,73–75]

Relatively to the washing process, the principles behind it are related with the difference in size between fibres and dirt particles. In terms of chemicals it does not differ much from flotation, being the main difference the use of higher amounts of surfactants instead of fatty acids. However, since washing removes a rather high amount of fillers, this process becomes rather relevant for the production of low ash pulp, which is often used for tissue paper production and other applications requiring such features.[70,73]

The combination of floatation and washing is often observed in some mills. The conjugation of the different deinking processes depends strongly on the fibre source composition and on the end-pulp desired features. Deinking processes based on floatation render higher yields and higher selectivity, comparatively to washing based deinking. The selectivity in both may be improved by applying one or more specialty chemicals. [73–75]

In general, washing displays high efficiency removing small particles (<10 μm), whereas floatation exhibits better results removing medium-sized particles (10–100 μm). As concerns larger impurities particles (>100 μm), screening and centrifugal cleaners are used.[73] These processes may occur either on alkaline or neutral environment. Alkaline deinking medium is widely used and considered more efficient for ink removal than neutral. However, it generates significant chemical oxygen demand, which is caused by the removal of carbohydrates and organic impurities from fibres.[70,73]

iv) Bleaching

Bleaching may be included on the deinking operations and it can be performed depending on the requirements desired on the end-product. It is a way to improve pulps

optical properties and add value.[70,74] Similarly to other operations, previously mentioned, bleaching conditions also strongly depend on the used fibre source (feedstock variability). In this process hydrogen peroxide is often applied as bleaching agent, due to its easy employment and low price. Additionally, since it does not degrade and remove lignin, it doesn't affect negatively neither the pulp yield (decrease) or the mill effluents (increase chemical oxygen demand COD, etc).[70,73]

A wide variety of chemicals may be used for bleaching. Besides chlorine free bleaching chemicals, such as, hydrogen peroxide (previously mentioned) or sodium dithionite, chlorine-containing chemicals (chlorine dioxide and sodium hypochlorite) have been used for wood free fibres, although these last have been abandoned due to environmental issues (formation of organochlorine compounds).[70,75–77]

In most cases the bleaching involves a two-stage process, consisting on an oxidation stage followed by a reduction. Even though in some cases these stages are sequential, overall something is added to end the oxidative action before the reductive stage starts. Examples of oxidative agents include hydrogen peroxide or oxygen, while the reductive ones are often sodium hydrosulfite and formamidine sulfinic acid (FAS). These are often used for bleaching and discoloration, and its use is rather relevant on fibre sources heavily contaminated with dyes and inks. [70,73,76,77]

The deinking operation lines comprise the combination of the techniques aforementioned and others, such as, screening (remove impurities), thickening (presses or belts used to increase pulp consistency), dispersion (detachment of contaminants and reduction of its particles to smaller sizes), or fine cleaning. [70,73,74]

After the deinking process, the pulp is ready to be manufactured into paper and related products. Some paper and board grades may be produced over recycled fibres exclusively. This can include corrugating medium and test liner, or newsprint. Other grades use blends of recycled and virgin fibres.[73]

As regards recycled pulp optical features, these are of utter importance in all cases, with exception of dark coloured board. In other cases, such as fine papers, newsprint or tissue paper production, high demands are required not only in terms of brightness but also in terms of low impurities specks count.[70,73]

Another parameter with high significance is the ash content. Depending on the pulps end-purpose, this parameter may be carefully controlled during deinking. An example of this would be the recycled pulp used for tissue paper manufacture. In this case, low ash content is required, not only due to process sensibility to high ash content, but also due to issues with end product desired features.[70,73]

The presence of stickies (such as glues, adhesives, etc) are another parameter to consider, since their presence is often associated with recycled paper quality.[70]

Besides the aforementioned, a good printability is also an important parameter as regards certain paper grades. Here, properties such as the fibre aptitude towards paper formation, fibres surface properties and papers strength are relevant. Additionally, properties such as water absorption and wet and dry strength are also rather essential, that is the case of tissue paper products.[70]

2.2.2.2. Recycled fibres quality

The expansion of recycled fibres utilization has driven a demand for a better comprehension about its nature and fundamental differences departing them from virgin fibres. As mentioned before, recycled fibres source is waste paper, whose features influence recycled fibres quality. Consequently, the different stages of waste fibres history, such as its origin or the processes they were subjected to, through its lifecycle, condition the produced recycled fibres properties. [78]

Cellulosic fibres can change significantly when formed in the wet web of paper and, subsequently, subjected to processes such as pressing, drying, printing, storage, repulping, and deinking. Often it is possible to replace recycled fibres by virgin ones, although their behaviour displays differences in terms of properties, such as lower hydration abilities, lower strength properties, etc. [69]

The presence of impurities is able to affect greatly recycled fibres properties. Even after deinking recycled fibres still exhibit significant amounts of impurities such as inks, glues, filler, fatty acids, etc. These affect fibres properties, such as its ability to bind and its hydrophilicity. However, the losses of intrinsic fibres properties (bonding ability, flexibility and swelling) are mostly attributed to the hornification effect. This phenomena limits significantly the application of recycled pulps in papermaking, especially in papers that require good strength properties.[79–81]

2.2.2.2.1. Hornification

Cellulosic fibres hornification consists in a series of structural changes on cellulosic fibres, induced, mainly, by successive swelling, pressing, and mostly drying operations. By subjecting fibres to such stressful conditions, rearrangements on cellulose chains occur, leading to the formation of irreversible hydrogen bonds between fibrils, yielding fibril aggregation, fibre collapse, substantial losses on fibres porosity, stiffening, inability to swell as originally, loss on fibre bonding capacity and, therefore, losses on mechanical and hydration properties. [79,82–84]

Hornification has been widely studied through the years and its consequences are of utter importance to pulp and paper industry, since drying and swelling are essential parts of the papermaking process, and the main guilty parties behind it. Besides, the on growing use of recycled fibres has made more and more essential a better comprehension of all the phenomena associated with losses on fibres quality, during its lifecycle.[85]

In general, the irreversibility of the hornification effect is related with the formation of irreversible hydrogen bonds. Cellulose displays a high amount of free OH groups, which allows the formation of interfibrillar bonds through hydrogen interactions. (Figure 2. 17).[82,85]

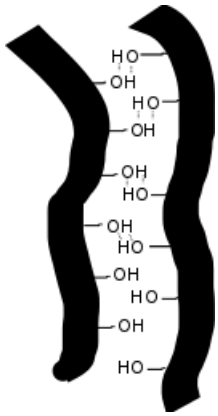

Figure 2. 17 – Hydrogen bonds between cellulose fibrils.

As results of the hydrogen bonding between external cellulose chains in fibrils, their aggregation takes place. Interactions between cellulose and water also play a relevant role, as concerns the supramolecular structure. Although not as strong as covalent bonds, due to high surface area and small distance between OH groups, hydrogen bonds, between cellulose chains, contribute significantly to the polymer supramolecular structure, which confer cellulosic fibres the ability to swell without dissolving in water.[85]

To explain the effect of drying (major cause of hornification) *Scallan*[84,86] proposed a model. In this model, an interpretation can be taken to what happens to microfibrils and its fibrils upon swelling, drying and re-swelling. The structure of dry cellulose consists on a set of microfibrils held together by hydrogen bonds, as shown in Figure 2. 18 (A). When in contact with water, water molecules interrupt interfibrilar hydrogen bonds, inducing fibrils to break apart initially into *B*, and further C and possibly D (Figure 2. 18). Upon drying fibrils return to structure A (Figure 2. 18). Although, upon re-swelling, due to hornification (presence of irreversible hydrogen bonds between adjacent microfibrils possibly formed during the drying process), fibrillar aggregation is verified, and therefore the microfibril structure expands less upon re-wetting, due to a lacking of free OH groups

available for interaction. Therefore, the microfibril structure instead of expanding further, as in C or D will be closer to B (Figure 2. 18).[84–86]

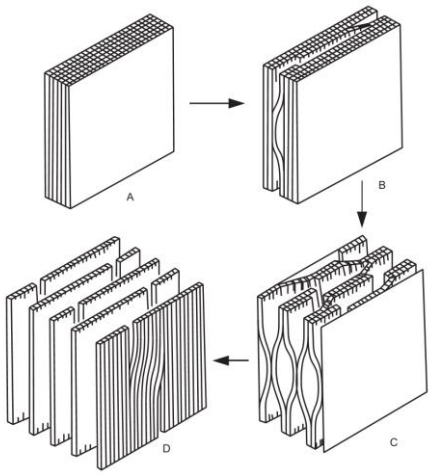

Figure 2. 18 – *Scallan* model(1977) (adapted from [85]).

The decrease of free OH groups caused by the hornification phenomena, has been investigated in the past [32–34]. It was demonstrated that the decrease of free OH groups, upon drying (cause of hornification), always leads to the decrease of accessibility.[85] As previously mentioned, hornification may be promoted/stimulated during certain process operations, such as pressing, drying, calendaring, printing, deinking, etc). During this operations, favourable conditions are gathered prompting the occurrence of hornification.[79,87]

Factors affecting hornification

i) Drying process

In pulp production and paper making the process of water removal from cellulosic fibres includes operations such as wet pressing, air drying or oven drying. High temperatures allow a rapid evaporation and thus removal of water molecules from fibres, which promotes structural rearrangements (different predisposition of fibrils) and the formation of irreversible hydrogen bonds, typical of hornification. The aggregation of fibrils and lower accessibility to free OH groups constitutes hornified fibres. Therefore, it is of general agreement that fibres hornification is highly affected by drying. Regardless of high temperatures effect, the water removal also contributes largely to fibres hornification.[82,85]

ii) Water amount in pulps

Water loss during drying also affects fibres hornification. When fibres are in contact with water structural changes are verified, and since water molecules disrupt bonds

between cellulose molecules, its mobility becomes less difficult, since there are less bonds holding them together. Small amounts of water (ca. 10-20 %w/w) allows to maintain the fibrils relatively disaggregated.The deep dehydration of pulp (less than 5%w/w residual water), leads to strong intermolecular interaction and fibrils aggregation. These changes are irreversible, because upon drying and re-wetting, pulps properties (hydration abilities and strength properties) differ from those from the beginning. Therefore, the formation of irreversible hydrogen bonds is promoted by exhaustive removal of water, bringing the aforementioned changes on fibres properties.[82,85]

iii) Fibres chemistry

Fibres composition plays an essential role on inter- and intra-fibre bondings which determine papers strength properties. Chemical (low yield) and mechanical (high yield) pulps differ from one another in terms of its fibres chemistry. While in the first most lignin was removed accompanied by some hemicelluloses (chemical process), in the latter most of its lignin matrix and hemicelluloses are kept (high yield).

In high yield pulps, the presence of high lignin and hemicelluloses contents benefits fibres, since these compounds act as barrier and protect cellulose-cellulose hydrogen bonds. By preventing the formation of irreversible hydrogen bonds, these compounds protect fibres from the hornification effect, being thus less prone to it.[79,81,84,85]

On the other hand, chemical pulps exhibit a high exposure of its OH groups (higher accessibility to free OH groups), due to the removal of lignin along with some hemicelluloses. This turns chemical pulps prone towards rearrangements, to the formation of irreversible hydrogen bonds and aggregation. Being susceptible to hornification, these pulps suffer losses on its fibres properties as result of hornification (e.g. hydration properties and strength properties). [79,81,84,85]

2.2.2.3. Treatments to improve recycled fibres

Recycled fibres suffer severe losses on their properties during their lifecycle, being only able to be recycled at most 3-5 times. However, these losses can be attenuated by a wide range of treatments. These treatments include mechanical (refining), chemical (such as alkaline solutions) and even biological treatments (enzymes). Alternative hypotheses include the mixture of virgin fibres with recycled fibres, or recycled fibres fractionation. Nevertheless, refining and alkaline treatment are the most common methods applied to improve recycled fibres properties. [78,79,81,87]

i) Refining

Fibre properties may be changed through a mechanical treatment widely used on papermaking, refining. Its main purpose is to further defibrillate fibres, which were collapsed with aggregated fibrils, and, thus, with less bonding potential due to hornification. The defibrillation produced by refining is expected to improve fibres accessibility, fibre bonding potential and thus its hydration and strength properties, which were compromised due to hornification. [78,79,81,87]

Although refining poses a good alternative to regain recycled fibres properties, it also causes fibres shorting, further fines creation and therefore lower freeness. Therefore, when refining recycled fibres it is important to bear in mind that during its history, recovered fibres have already suffered refining and that recycled pulp has fibres that may be more prone to fragmentation. Thus, refining parameters should be carefully controlled, in order to decrease, as much as possible, the negative effects coming from its use. To attenuate such effects, low intensity refining or high consistency refining may be used.[79,81,87,88]

ii) Blending

Recycled fibres properties can also be upgraded by blending with other fibres, such as virgin fibres. Due to recycled fibres low bonding ability, stiffness and thus frailer mechanical properties, virgin fibres, in a certain proportion, are blended with recycled fibres. Virgin fibres do not exhibit low bonding ability like hornified fibres, thus they confer to the blend higher bonding ability, yielding stronger fibres network and thus strength properties. This is especially true when it comes to blending with refined virgin fibres. [78,79,87]

iii) Fractionation

The technique of fractionation mostly applied during the paper recycling process, is used as a way to upgrade recycled fibres performance. It does not reverse the effect of hornification on recycled fibres properties, but, since it separates different types of fibres in the recycling process, it attenuates the losses in terms of its papermaking properties. [78,79,81,87]

Fractionation improves pulp quality and allows a better control of pulp and paper characteristics by redistributing its fines and ash. Usually it is easy to find utility for the long fibre fraction, although the same is not exact when it comes to the short fibres fraction and stickies.[78,79,81]

iv) Chemical treatments

Different approaches may be followed; i.e. chemical treatments may be applied either with the intension of preventing hornification or to improve fibres properties degraded by hornification. [79,81,87]

An example of prevention treatments includes the chemical modification of cellulosic fibres, before papermaking, by partial substitution of cellulose OH groups. These methods aim to avert the formation of the irreversible hydrogen bonds, characteristic from hornification. These methods consist, in most cases, on cellulose derivatization which includes methylation, acetylation or even carboxymethylation reactions. [79,87]

Chemical additives may also be added as a way, not to prevent, but to improve/reverse hornification. Alkaline solutions are a rather popular treatment in papermaking to improve recycled fibres properties. After refining is the second most reliable method to retrieve recycled fibres properties. The treatment of recovered fibres with sodium hydroxide (high pH conditions) aims, mostly, to improve fibres swelling, freeness and its strength properties. It has demonstrated better results, in some cases, than even refining, however, in the next recycling cycle fibres will be more affected by hornification. Alkaline treatment may be conjugated with refining to further improve recycled fibres properties.[79,81,88]

v) Enzymatic treatment

In the last decades, the use of enzymes on paper recycling processes has demonstrated great potential as an environmentally friendly addition for the deinking process. The use of enzymes during paper recycling aids not only impurities removal and bleaching, but also improving recycled fibres drainability and strength properties. [81,89,90]

Enzymes action during deinking generally occurs either by attacking the ink/impurities or the fibre surface on the fibre-ink interface. Enzymes can be used separately or in conjunction, to optimize the deinking process. Pectinases, hemicellulases, cellulases and other ligninolytic enzymes act on the fibre surface or bonds close to the ink particles, freeing the ink for removal. Lipases and esterases act by degrading inks based on vegetable oils.

Ligninolytic enzymes action, besides removing impurities, also may improves fibres strength properties (higher bonding ability) and drainability.[81,89–91]

Cellulases are widely used to facilitate the deinking of waste paper. Its action peels fibres, which, besides aiding impurities removal, also improves fibres bonding ability (fibre are more fibrillated) and its freeness (fines degradation). Cellulases may also be used

in conjunction with hemicellulases. Hemicellulases may also be used alone without cellulases. An example of a widely used enzyme on pulps biobleaching is xylanase. Additionally, this enzyme, due to its ligninolytic nature, may modify fibres to be with properties near those of slightly beaten. [90–93]

Enzymes represent thus a great opportunity to improve recycled fibres quality and turn more efficient the paper recycling process. By applying the appropriate enzyme cocktail, under optimum conditions, it is possible to improve deinking, drainability, stickies control and "refine" pulp (energy savings). [81,90,94]

2.3. Paper products - Tissue papers

Pulp is used as main source to produce a great variety of products with numerous applications. Examples of products manufactured from pulp include office paper, newspapers, magazines, books, packing products, tissue paper, etc.[54] Despite the huge variety of pulp end uses this work will only be focused on tissue paper manufacture.

Tissue paper consists on a low weight creped paper, widely used by society for domestic, sanitary and industrial purposes. Tissue is often made in weight ranging from 8-50g/m^2 with a porous elastic structure, with a good absorption ability and high softness. It can be made from both virgin and recycled fibres, as mentioned on the previous sections, and used to produce a wide diversity of products such as toilet paper, facial tissue paper, paper towels, napkins, etc.[95,96]

2.3.1. Tissue paper production

Tissue paper is usually produced by a mixture of hardwood and softwood pulps; whose proportion depends from paper mill to paper mill. Recycled pulp is normally used to produce recycled based tissue products, but essentially in conjugation with virgin fibres. [95,96]

General paper production process consists of the following stages. Initially, stock is prepared by dispersing pulp in water and additives. Pulp suspension is then supplied on a former section, where water is removed by gravity or vacuum. Afterwards the wet paper web enters the press section where further water is removed mechanically (dry solid content of 33-55% depending on the type of paper). The remaining water is removed by drying, on a drying section, which could be done by one or more stages depending on the paper grade.[97]

Even though the principles behind paper machines are much alike they still exhibit differences in terms of individual components, which is related with the type of paper produced.[96–98]

In tissue paper production the sheet formation process in many cases still consists on a fourdrinier wet-end, which entails many operations such as stock delivery, sheet formation, water removal, low vacuum and high vacuum. Other technologies include gap formers or crescent formers. For example, in a conventional tissue machine the paper web is formed in a gap former, transferred by the felt to the dryer section, where first is pressed and mechanically dewatered by a shoe press acting against the tissue cylinder.[98,99]

In the drying section, two types of processes may be encountered. In conventional wet press process (CWP), the dryer section includes a Yankee dryer section, which is the most traditional drying technology. Although in recent years the through air drying, TAD, technology arose as an alternative. [96,98,100]

In the typical CWP process the paper web is formed, then transferred to a felt and dewatered by pressing against the Yankee dryer. The pressing allows the paper web to be transferred into the Yankee dryer surface, where an adhesive was sprayed prior to the sheet formation to provide good adhesion between the paper sheet and the Yankee dryer surface. The Yankee dryer consists on an iron cylinder (Yankee cylinder) with a diameter of 5-7m, heated with steam from the inside, to dry the paper web passing at high speeds outside. The paper web is dried and is then removed by a steel blade, "the blade doctor", which produces a creped elastic sheet. The creping process is controlled by the strength of the adhesive on the Yankee cylinder, the geometry of creping blade, the speed difference between the Yankee and the final section of the paper machine and pulp features. [95,96,100]

The creping process decreases sheet density, increases strength, and thus softness along with good absorbency features, which are typical on tissue paper products. After creping, the paper sheet obtained is subsequently made into tissue products. [100]

The TAD process consists on another drying process, which is used to produce extra soft and absorbent tissue paper. In this process the paper web is dewatered and pre-dried, without mechanical pressing, which preserves bulk. Hence, the paper web is formed and then transferred to the porous TAD-cylinder, in this case, into the TAD-wire, where the paper web is dried by blowing hot air through the paper sheet and the felt. This creates on the paper sheet high and low weight regions and high and low density regions, dispersed through the fibres network. After a pre-drying TAD process the paper sheets may be subjected to a Yankee dryer and creping, for higher strength, softness and absorbency.

Even though tissue made from TAD is uncreped it is useful in some applications, creping is mostly commonly used for towel and tissue grades, particularly premium grades. [98,100]

Even though TAD has become rather popular due to its higher absorbency, softness and bulk papers, the process requires the consumption of tremendous amounts of energy (twice the energy of conventional drying process). In Figure 2. 19 it is possible to observe the illustration of a conventional tissue paper machine, while on Figure 2. 20 it is represented a tissue paper machine with TAD process.[95,96]

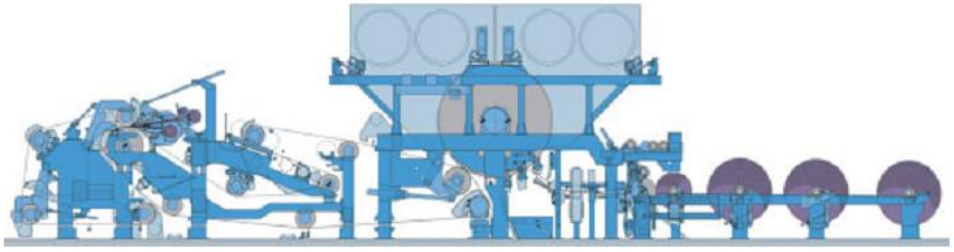

Figure 2. 19 - Conventional tissue paper machine.[98]

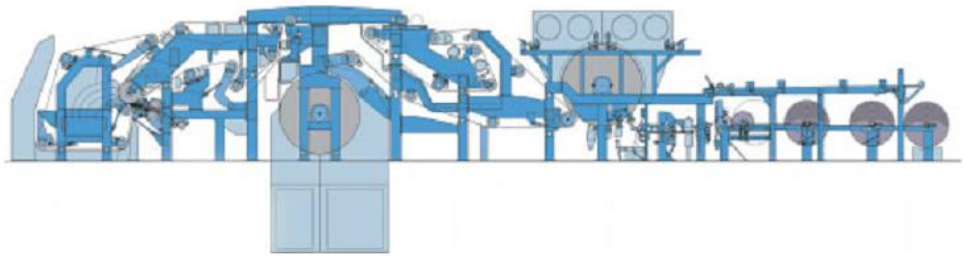

Figure 2. 20 - Tissue paper machine with TAD process for the production of extra soft tissue paper.[98]

2.4. Additives – Product differentiation

In tissue paper products aesthetic, tactile and absorbency properties are given major relevance by consumers. Products appearance is rather relevant, however its tactile perception, i.e. softness, and water absorption capacity are yet fundamental features to the consumer's eyes. These properties may be adjusted by process variables, or improved further by the addition of additives. [100,101]

Additives may be applied to either improve already existing paper properties, such as its hydrophilicity or softness, or to confer new differentiating features. This is the case of additives able to confer features such as colour, odour or even antimicrobial properties. These new features, besides allowing tissue paper to differentiate from conventional tissue paper products, turns them more appealing and special towards consumers. Examples of additives applied to achieve the aforementioned properties include humectants (improve hydrophilicity and softness), dyes (confer colour), antimicrobial agents (antimicrobial properties) or even perfumes (pleasant odour). [102,103]

2.4.1. Humectants

Due to cellulosic fibres high affinity for water, paper is used to manufacture a wide variety of absorbent products. As mentioned in previous sections, cellulose is able to interact with water and form hydrogen bonds. However, the amount of water that cellulosic fibres are able to absorbs varies and is influenced by cellulose accessibility (as previously mentioned) and thus by fibres porosity or even its composition.

In tissue manufacture to improve papers water absorption capacity, changes on the process may be applied. As early mentioned, TAD drying and creping operations influence greatly tissue paper absorbency. For example, creping plays a key role on tissue paper water absorption. The process induces crinkles on tissue paper, which breaks many interfibre bonds, which were previously formed during drying. This operation changes tissue paper topography, which results on much higher surface area and thus more sites available for interaction with water. Additionally it also turns tissue paper softer.[96,98,100]

Besides mechanical operations, in tissue and other hygienic and cosmetic products, chemical additives, otherwise denominated as wetting agents, humectants or moisturizers may be added to further improve both water retention/absorption and softness properties. [104,105]

In products such as cosmetics or food packing its composition often includes humectants. Humectants attract and hold on to water. Thus these materials are applied, in a wide variety of products, either to retard water loss or to increase its uptake. This task is usually performed by substances of hygroscopic nature. Example of humectants often used on cosmetic products include pyrrodilone carboxylic acid, urea, panthenol, butylene glycol, propylene glycol, glycerine, polyethylene glycol, and other inorganic ions.[106–108]

Humectants can be divided into three groups, inorganic, metal-organic and organic. Both metal-organic and organic humectants are frequently applied on the manufacture of hygiene and cosmetic products, while the same is not valid for inorganic humectants. [108]

i) Inorganic humectants

Inorganic humectants consist on salts of inorganic acids. Calcium chloride is an example. These type of humectants find little use on personal care products due to problems related not only with its corrosive action, but also with problems such as destabilization of emulsions in creams, decreasing foam, etc. [108]

ii) Metal-Organic Humectants

Metal organic humectants, as denoted by its designation consist on a mixture of a metal ions and an organic counterpart. These humectants are rather useful and include compounds such as sodium lactate or sodium PCA (pyrrolidone carboxylic acid). [106,108]

iii) Organic Humectants

Organic humectants are extensively used in the cosmetic industry. This class of compounds includes glycerol, ethylene glycol, polyethylene glycol (PEG), propylene glycol, glycerine, urea, sorbitol, etc. Their strength as humectants depends strongly on their ratio of OH to carbons, hence increasing ratio increasing hygroscopy. [106,108]

The changes produced on a material hydrophilicity by the addition of hygroscopic agents, namely on paper products can be accessed by many tests. In case of tissue paper this analysis can be performed considering ISO 12625-8:2010 (Tissue paper and tissue products - Part 8: Water-absorption time and water-absorption capacity, basket-immersion test method) and ISO 8787:1986 (Paper and board - Determination of capillary rise - Klemm method). The first test is extensively used on tissue paper industry and it allowed to determine the quantity of water a certain amount of paper is able to absorb, along with the time of absorption. As regards ISO 8787:1986, its used has been abandoned through the years by replacement with ISO 12625-8:2010.

A material hydrophilicity may also be accessed through contact angle analysis. Although not common for tissue paper this analysis is widely used to investigate materials wettability.

2.4.2. Dyes

Colour of objects (e.g. paper) is only possible due to the interaction of light with matter. When light is shone upon it, part of that light will be absorbed, while the other will be reflected. It is this light, the reflected part that will enter human eye and send a signal, which the brain interprets as colour. Humans are only perceptive towards a small portion of the electromagnetic spectrum, the visible region, between 400 and 700 nm. [109,110]

It is of common understanding, that when light is completely reflected, to our eyes the colour appears white, whereas if all is absorbed it appears black. Additionally, when light is reflected throughout the whole visible spectre the object appears grey. Nevertheless, if light is partially absorbed, as in a short wavelength range (e.g. 435-480nm, blue light), then chromatic colour appears (in this case yellow). In Table 2. 5 it is possible to observe the different regions of the visible spectrum, the colour of light at that specific wavelength band and the shade which will absorb that particular wavelength. All shades

can be represented by a reflectance spectra, which works much like a fingerprint. [109,111]

Table 2. 5 – Wavelengths of light and the colour it absorbs. [109]

Wavelength (nm)	Colour of this light	Colour which will absorb this wavelength
400-435	Violet	Greenish yellow
435-480	Blue	Yellow
480-490	Greenish blue	Orange
490-500	Bluish green	Red
500-560	Green	Purple
560-580	Greenish yellow	Violet
580-595	Yellow	Blue
595-605	Orange	Greenish blue
605-700	Red	Bluish green

To convey colour to paper, cellulosic fibres are treated with dyes. The selection of the most appropriate dye to impregnate cellulosic fibres depends, mostly, on the end-products purposes, its desired physic-chemical properties, its features or manipulation. Overall, dyeing is expected to confer paper a specific shade or tonality .[110]

There is a wide variety of dyes able to absorb light at different wavelengths and therefore bestow different colours to paper products. Dyes can be classified according with its chemical structure (e.g. azo, anthraquinones, etc) or its application method, the classification by colour index (acid, basic, direct dyes, etc). The former classification is commonly used by the dye chemists, while the latter is mostly used by the dye users. [111,112] Even though being quite common, both classification may be mixed together to designate a dye (for example, direct azo dye or anthraquinone acid dyes).[111,113] However, here it will only be introduced the colour index classification, which is the most common among its users, such as the paper industry.

2.4.2.1. Colour Index classification

The colour index classification, i.e. dye classification according with its use or method of application, may be advantageous on the eye of users, relatively to classification by chemical structure. In this system of classification, dyes are divided into groups such as basic dyes, acid dyes, direct dyes, sulfur dyes, pigments, reactive dyes, vat dyes, disperse dyes, mordant dyes, etc. Although, in paper industry, the most common are direct dyes (Figure 2. 21).[110,112]

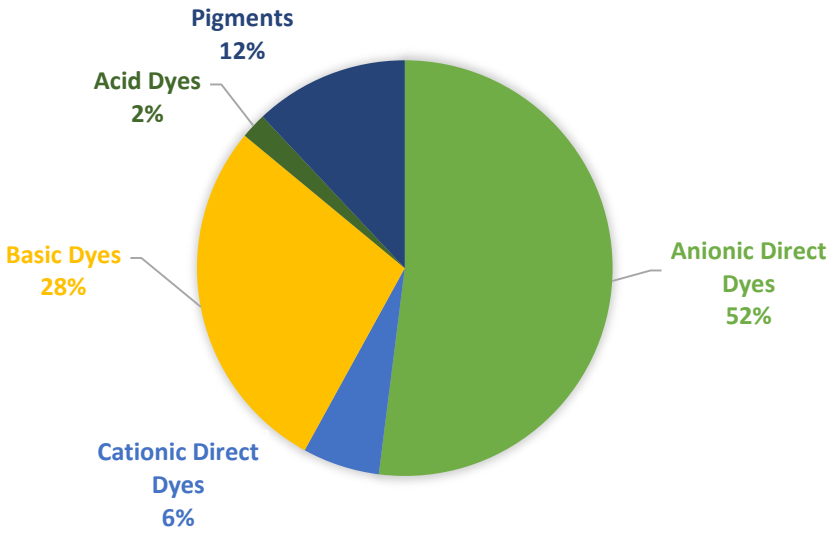

Figure 2. 21 – Relevance of the different classes of dyes in 2004 (adapted from[110]).

i) Basic Dyes (Cationic dyes)

Basic or cationic dyes consist mostly on salts (chlorides, hydrochlorides, sulfates, and oxalates) of colour bases.[109,110,113] Some of older basic dyes consisted on di- and triphenylmethane, heterocyclic azine, oxazine or polymethine, or aminoazo compounds.[114] These dyes are not water soluble and sometimes require de addition of acid, to produce dye solutions. Acetic acid is often used on these formulations. [109,110] Basic dyes are frequently employed on the coloration of materials with anionic nature, where strong electrostatic attractions may be established. Examples of such materials include protein fibres (e.g. wool, silk and leather), synthetic polyamides (such as nylon) and pulp containing lignin (e.g. unbleached pulp or ground wood). Additionally, these dyes (high cationic charge) also exhibit a high attraction towards fillers. [110,111,114] Conversely, bleached pulps affinity with basic dyes is very poor, and for that reason these dyes are often not considered suitable for these materials coloration. [111] Even though its use is decreasing on paper industry, these dyes are still used on the production of packing papers (liner, testliner, corrugating medium), or wood-containing printing/writing papers.[109,110]

To improve dye fixation anionic fixatives may be added (for example, sodium salts of condensation of formaldehyde, naphthalene sulfonic acid). The use of fixatives is usually related with bleached pulps dyeing, which contain very low amounts of lignin. They allow an enhanced dye fixation, richer colours, along with improved bleedfastness. Moreover, since dye fixation is more efficient, effluents become less stained.[110]

Basic dyes usually exhibit brilliant colour and advantageous dyeing costs. They also display good fastness to water and steam on lignin containing materials (due to their good fixation on these materials). [109,110] However, despite the referred benefits, the disadvantages associated with its use include the already mentioned poor affinity towards

bleached materials, mottling tendency (which affects the uniformity of the dyed material) and poor light fastness. Many of these dyes are becoming obsolete, but a few are still used for dyeing paper, leather and for inks manufacture. [109,114]

ii) Acid Dyes (Anionic dyes)

Acid dyes or anionic dyes are water-soluble salts of organic acids (often potassium or sodium salts). Most acid dyes are azo dyes and are quite similar to direct dyes. They contain one or more water-solubilising anionic groups, mostly sulfonic acid groups of sodium salts. When in water they dissociate into coloured anions. [110–112,115]

Although basic dyes exhibit high solubility, more sulfonic acid groups on their structure (meant to improve solubility) may cost these dye's affinity and/or substantivity for their substrates, yielding thus poor bleed fastness or coloured effluents. An example would be its poor affinity towards cellulosic fibres. Even though acid dyes are able to diffuse inside fibres, the use of fixatives is required (often aluminium sulfate and cationic fixative agents, such as condensation products of dicyandiamide with formaldehyde, polyamines, polyvinylamines). [109–111] Since cellulose is anionic in aqueous medium, dyes may be only attracted by means of hydrogen bonding or through Van der Waals forces. To prompt that situation, it is rather important that dye molecules approach very closely cellulose molecules, for what dye molecules linearity and/or planarity is essential. [111]

These dyes are of limited use in paper industry and are mainly applied on textile fibres with cationic character, such as protein fibres (wool, silk and leather) or synthetic polyamides (nylon). [111]

Further disadvantages include strongly coloured effluents and poor bleed fastness. Advantages of acid dyes are their solubility, no tendency to mottle on stock mixtures, and its suitability for dip and surface dyeing. Acid dyes are mainly used for certain types of paper, decorative crepe paper, and carbon paper. The importance of acid dyes for paper dyeing has decreased greatly not only due to its poor cost/performance ratio but also due to the aforementioned effluents issues. [109–111]

iii) Direct Dyes

In paper industry, direct dyes otherwise known as substantive dyes, are the most important and extensively used dyeing materials. These dyes are divided into cationic and anionic, as demonstrated by Figure 2. 21. [110,111] As the name suggests, substantivity (the ability to absorb onto fibres from an aqueous medium) is here an essential requirement, along with affinity (the ability to become bound to the fibre). [111,116]

Anionic direct dyes

From all direct dyes, anionic dyes are the far most widely used on tissue paper production, and on printing/writing paper production. These dyes are quite similar to acid dyes and their structure includes groups responsible for enhancing water solubility, mostly $–SO_3$. Due to their larger, linear and/or planar molecular structure they have a higher substantivity and affinity towards cellulose, relatively to acid dyes. [109–111]

Most anionic direct dyes are polyazo dyes, with structures consisting, mainly, on azobenzene, naphthalene, biphenyl, stilbene and aromatic heterocycles. Another group are copper phthalocyanines. Due to these molecules structure, it becomes easier to get closer to cellulose molecules and interact with then (through hydrogen bonds, Van der Waals forces, and/or hydrophobic interactions). They exhibit good affinity towards bleached chemical pulps and they may be applied over a wide pH range, yielding good fastness properties. [110,111]

Fixatives or fixing agents are added to achieve deep shades with good bleed fastness (e.g. deeply coloured napkins). Inside the fibre, the cationic compounds precipitate the anionic dyes, still in solution, by forming with dyes higher molecular mass aggregates, with lower solubility, which causes its precipitation inside fibres. Therefore, dye removal becomes more difficult. These additives consist mainly on quaternary ammonium compounds and cationic formaldehyde condensation resins. These dyes are not suitable to wood containing feedstocks, since wood components prevent a uniform dyeing process. Its lightfastness is usually good, but the colour attained may not be as brilliant as that on acid and basic dyes. [110,116]

Cationic direct dyes

Cationic direct dyes, alike anionic direct dyes, display a planar molecular structure, but with cationic groups. The cationic charge, when compared with anionic charge (water solubility and repulsive forces), allows an improved attraction between fibres and dye molecules, and thus an excellent dye fixation. Due to the anionic character of cellulose in water, a cationic dye can form strong electrostatic interactions besides the usual weaker hydrogen bonds, or Van der Waals'. [109–111]

There are many types of cationic groups besides quaternary ammonium groups. These dyes molecules may contain pyridinium pyridine, thiazolium, benzthiazonlium, indolium and triazolium cationic groups. [109–111]

Conversely, the presence of positive charges does not favour the dyeing process of mechanical fibres. When this is not the case, these dyes originate good bleedfastness and their combination with anionic direct dyes may be used to enhance dye fixation.[109,110]

iv) Other dyes

Other classes of dyes include sulfur dyes, pigments, reactive dyes, vat dyes, disperse dyes, mordant dyes, etc. While the first two are still applied to cellulosic fibres to a small extent, the others find little or no use in paper industry. Although they may be applied to cotton or other fibres (wool, silk, etc) coloration on textile industry. [110,111,113]

2.4.2.2. Influences on the dyeing process

The dyeing process can be influenced by many aspects, such as the fibres chemical composition, dyes substantivity and affinity towards cellulosic fibres, type of forces established between dyes and fibres, process conditions (e.g. temperature, agitation, pH, and others), etc. [111]

As previously referred the feedstock composition can influence fibres dying process, since different types of pulp (bleached or mechanical pulps) display different affinities towards the same dye. This sensibility towards stock variations, may create issues as concerns the dye fixation, which often requires the use of chemical additives, such as fixatives to settle these setbacks. Moreover, pulp refining also influences fibres dying. If fibres were previously refined shade variations may occur, since beaten and fibrillated fibres are more accessible towards dyes relatively to unbeaten ones.[109,111,117]

Other process conditioning parameters include pulp consistency (could originate non uniform coloration), water hardness (helps reducing repulsive forces between fibres and dyes), fillers content (consumes dyes and gives weaker depths of colour), fixatives (cationic products added to aid dye fixation), and moist content (certain dyes are affected by moisture yielding changes in shade). The order of additives addition (dye, fixatives, etc) also plays a rather relevant role on the dyeing process, being able to affect greatly the dye fixation, the products colour uniformity, etc.[109,111,117]

The type of dyes selected may also influence the process. Its substantivity and affinity play a key role on the process. Substantivity consists on the ability of the dye to be absorbed by cellulose fibres from an aqueous medium, while affinity is the capacity of the dye to be bound to the fibre. Therefore, if a dye possesses high substantivity, due to low affinity it may exhibit poor fastness. Similarly, a dye with low substantivity and high affinity will create coloured effluents, but good fastness properties. It is thus essential,

during dye selection, to look for dyes with both high substantivity and affinity for fibres, for a more efficient process. [111]

The interactions existing between dye and fibres also affect dye fixation and fastness properties. Generally, the dyeing process starts with the dye migration towards the fibres interface followed by its adsorption. Then the dye molecules diffuse from the surface into the fibres interior. Afterwards, dye molecules are fixed to fibres, either by hydrogen bonds, covalent bonds, or other type of physical interactions, depending on the type of dye and other materials involved on the dyeing process. [113]

This process may also be conditioned by electro-potential forces, temperature and agitation. When immersed on water or aqueous solution every fibre exhibits a certain electric potential, usually designated as zeta potential. For example, cellulose, exhibits negative charge when immerse in neutral solution. Given the case of acid dyes or even anionic direct dyes, in solution, these are negatively charged. Therefore, they will be repelled by the opposite charge, such as the case of cellulosic fibres. On the other hand, being the substrate wool (proteins), under its isoelectric point, it displays positive charge, therefore this substrate will be attracted towards negatively charges dye molecules. [113,118]

When there is a mutual repulsion between the fibre and dye, higher times are required before the inherent vibration to the molecules in solution have brought them near enough cellulosic fibres. The problem, therefore, is to accelerate the migration to the surface of the fibre. This may be achieved by increasing temperature, which promotes vibrational activity, and also by the addition of electrolytes that counteract the effect of the negative zeta potential. [113]

The effect of agitation is only apparent, when the amount of dye in the solution is limited. Under such conditions the diffusion into the fibre could be quicker than the assembly at the surface and agitation will then become a significant factor. The rate of diffusion into the fibre is obviously dependent upon the concentration of dye in the interfacial layer, this can under certain conditions be influenced by the degree of agitation. [113]

2.4.2.3. Colour evaluation

To attain a certain shade, one or more dyes (mixture) may be used. Liquid or powder dyes are stored and them pumped (dye dilution is often required) automatically into the stock. Afterwards, the colour of the produced papers is analysed by a colorimeter or a spectrophotometer to evaluate if the produced shade agrees with the desired one. If not

adjustments on process variables have to be performed.[111] The colour evaluation is often performed by analysis of samples colour space coordinates and *K/S* values.

i) CIE L*a*b colour space coordinates

Human eye is not able to quantify colour accurately, thus colour measurement is essential for matching coloured samples, determining colour differences and adjust dyeing parameters. Understanding the fundamentals of colour measurement, or colorimetry, is essential for the optimum use of this technology.[119]

Space colour coordinates are used as a way to express colour. CIE "Commission Internationale de L'Eclairage" (light and colour science authority) has defined three colour space types, CIE XYZ, CIE L*C*h and CIE L*a*b*. Being this last the most extensively used. [109,119]

In CIE L*a*b space coordinates every colour is described by three coordinates L*, a* and b*. L* represents the samples lightness/darkness, while a* represents the degree of red/green, where +a* implies a redder colouration and –a* a greener colouration. As concerns b*, this last represents the degree of yellow/blue where +b* is indicative of a yellower colouration whilst –b* indicates a bluer one. [109,119]

Considering the abovementioned coordinates system, it is possible to perceive that neutral shades (whites, greys blacks) will be positioned near the L axis, although not all white papers imply L*=100 neither black paper imply L=0. [109,119]When a certain colour such as red or yellow is added, it possible that L* will be reduced (since the amount of light reflected is lower) and a* and b* coordinates will vary accordingly with the added colour. For example, if red is added, a* will increase (+a*), while blue will originate a development of –b*.[109,119]

Simplistically, if a red colour is added, this will result in an increase in the +a* value, whilst a blue colour will result in an increase in the –b* value. [109,119]

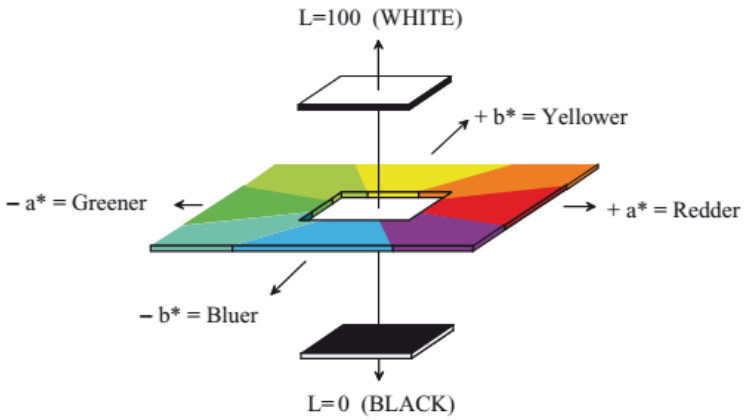

Figure 2. 22 - CIE L*a*b system.[109]

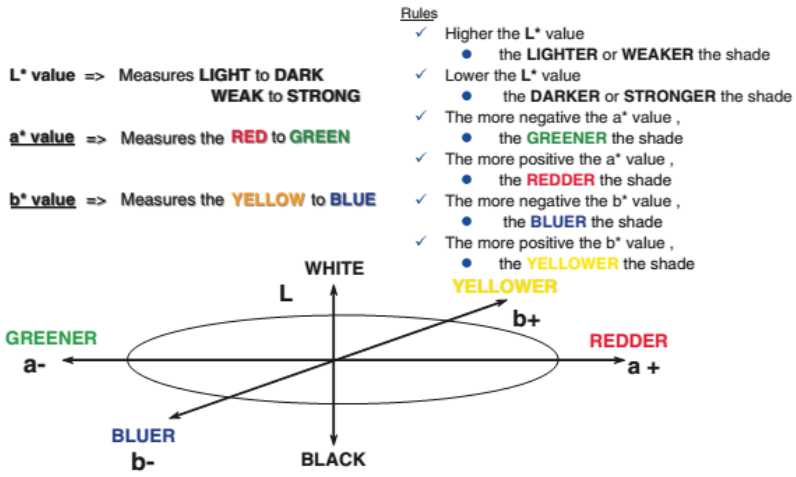

Figure 2. 23 - Schematic explanation of the model. [109]

To analyse the produced shade of colour with the desired one the colour coordinates are used to determine the colour differences, which are defined by the absolute difference between the samples and a reference sample. For each coordinate this difference is named delta (Δ), as may be either negative or positive. The ΔL* parameter represents the difference as regards coordinate L*, which suggests if the samples are lighter (positive) or darker (negative), relatively to the reference. On the other hand, Δa* describes the difference between red and green, i.e. if the samples are redder (positive) or greener (negative), while Δb* defines if the samples are yellower (positive) or bluer (negative). [109,119,120]

The total colour difference between all three coordinates is named ΔE*. The determination of colour difference is usually derived through the CIELab 1976 equation (Equation 2.15).[109,119,120]

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad \text{Equation 2. 15}$$

It is possible to establish a connection between ΔE and the human eye. This correlation is represented in Table 2. 6, where ΔE values are related with a standard observer perceptions.[120]

Table 2. 6 – Generic correlation between ΔE values and a standard observer perception. [120]

ΔE	Perception
0 – 1	The observer does not notice the difference
1 – 2	Only experienced observer can notice the difference
2 – 3.5	Unexperienced observer also notices the difference
3.5 – 5	Clear difference in colour is noticed,
Larger than 5	Observer notices two different colours

ii) Kubelka-Munk model

Colour may also be analysed quantitatively. For opaque materials Kubelka-Munk equation[121] correlates a sample's spectral reflectance (R%), its absorption (*K*) and its scattering (*S*) features. Kubelka-Munk relationship is given by Equation 2.16, where *K* is the coefficient of absorption, *S* the coefficient of scatter and *R* the reflectance of the sample at a given wavelength. To a first approximation *K* and *S* are proportional to the concentration of each dye in the substrate.[119,122–124]

$$K/S = \frac{(1-R)^2}{2R} \qquad \text{Equation 2. 16}$$

This relationship is rather useful when formulating colours on textile, coatings and paper industry. In these cases, it is presumed that the scattering (*S*) of a dye depends on the properties of the substance, whereas absorption (*K*) of light depends on the properties of the dye. The value of *K/S* is considered to have a proportional relationship relatively to dye concentration (C) on the material (equation 2.17).[123,125]

$$K/S \propto C \qquad \text{Equation 2. 17}$$

This assumption is considered when intended to relate a materials appearance with the kind and amounts of dyes in it. This parameter plays an essential role on products colour formulation. The colour yield of dyeing is the depth of colour that a unit mass of dye is able to impart to the dyed substrate. It can be assessed visually, but a more quantitative measurement is possible using the Kubelka–Munk *K/S*.[122,124,125]

2.4.3. Antimicrobial agents

Consumers concerns and thus demand for antimicrobial products, as a way to contain microorganism's contamination has driven the development of new differentiated products, with antimicrobial features. [126,127] An example would be the case of tissue papers, namely Cascade's new antimicrobial tissue paper.[128,129]

Tissue papers being made of natural fibres (cellulose) are susceptible to microorganism's life and growth, however the use of antimicrobial agents is a way to prevent its growth and propagation, which may result in sanitary issues or harm human health. [126,127]

Antimicrobials may differ in terms of chemical structure, effectiveness, method of application, influence on people and on the environment, as well as on cost.[126,127,130]

To obtain an effective action, an ideal antimicrobial treatment should meet a few requirements, such as being effective against a broad spectrum of bacterial and fungal species, but also, at the same time, display low toxicity to consumers. It should also be durable (be active for a long period of time). It must also be compatible with the chemical

processes, in which it will be included, be cost effective and not be harmful to either the manufacturer or the environment. [131,132]

Antimicrobial agents either inhibit the growth (-static) or kill (-cidal) the microorganisms. For example, antimicrobial agents used in commercial textiles, e.g. silver nanoparticles, triclosan, polyhexamethylene biguanide (PHMB) and quaternary ammonium compounds, are biocides. They act either by damaging microorganisms cell wall or alter cell membrane permeability, denature proteins, inhibit enzyme activity or inhibit lipid synthesis, all of which are essential for cell survival.[130,131,133–136]

Antimicrobial agents are already employed in many different areas and materials. They are used as food preservatives, disinfectants, swimming pool sanitizers or in wound dressings. Although these agents exhibit a powerful bactericidal activity, their attachment to fibres (such as cellulosic fibres) may reduce its activity and limit its availability. For these reasons, higher amounts of these compound need to be applied to control bacterial growth and to preserve the antimicrobial activity for longer periods.[126,131,137]

Some antimicrobials investigated or used on textile industry, the closest to the tissue industry, include quaternary ammonium compounds, N-halamines, chitosan, halogenated phenols (well-known triclosan), polybiguanides, nanoparticles of noble metals and metal oxides, and plant based antimicrobial agents (e.g. polyphenols, essential oils, etc).[131,138–140] Despite the wide variety of possibilities, only PHMB will be further discussed, because it was used in the present work.

2.4.3.1. Polybiguanides

Polybiguanides, are an example of effective antimicrobial agents, which consist on polymeric polycationic amines, with cationic biguanide repeating units separated by hydrocarbon chain linkers of identical or dissimilar length. [126,137,140]

Polyhexamethylene biguanide (PHMB) is a well-known strong and broad spectrum antimicrobial agent with low toxicity, which has attracted the attention for antimicrobial finishing in textile industry, mainly for the protection of cellulose fibres. This compound is frequently used as a disinfectant in the food industry and in the sanitization of swimming pools. It is also being explored as a biocide in mouthwashes and wound dressings. [131,137,140,141]

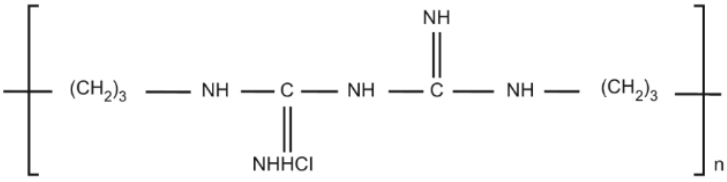

Figure 2. 24 – PHMB chemical structure.

PHMB acts by undermining the integrity of the cell membrane. Its cationic molecules interact with the anionic phospholipids in the microbe's cell membrane, increasing its permeability to the point of its disruption, which ends with cells' death.[133–136,138]

PHMB antimicrobial activity increases with increasing degree of polymerization, which is related with the higher number of sites (biguanide units) available to interact with microbe's cell wall. However, as higher is the molecular weight, the lower is the solubility of PHMB.[126,131]

PHMB cationic nature allows it to interact with cellulose, not only through hydrogen bonds, but also through ionic interactions. In literature it is mentioned that PHMB can bind to cellulose through its anionic carboxylic groups. As mentioned before, besides promoting a higher antimicrobial activity, polymer length also provides more cationic sites, for interaction with cellulose, and thus a stronger binding. For low concentrations electrostatic interactions between PHMB and carboxylic groups in the cellulose are dominating. However, with increasing of PHMB concentration, hydrogen bonding between PHMB and cellulose, becomes dominating, and thus multilayer adsorption is preferential. [131,140,141]

2.4.3.2. Functionalization with antimicrobials

Antimicrobial features may be conveyed to materials by functionalization of those with antimicrobial agents. In case of synthetic fibres, antimicrobial agents may be added before extrusion rendering synthetic fibres with antimicrobial features. In other cases, such as natural fibres (e.g. cellulose), antimicrobial agents are applied to fibres by impregnation. Then, this agents get attached to fibres either by formation of covalent bonds, electrostatic interactions, hydrogen bond or Van der Waals interactions.[130,138]

Another approach for the functionalization of materials with antimicrobials, includes the use of encapsulated antimicrobial agents, for posterior application on fibres. [142]

Microencapsulation is defined as a technology of packaging solids, liquids, or gaseous materials in miniature, sealed capsules that can release their contents at controlled rates under specific conditions (example Figure 2. 25). [142,143]

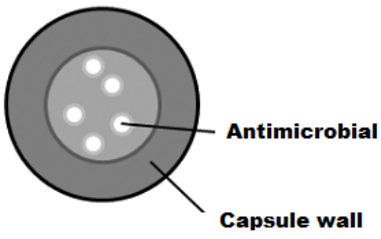

Figure 2. 25 – Schematic representation of a capsule containing antimicrobial compounds (adapted from [144]).

In the case of textile industry, the closest to tissue paper, encapsulation is used for durable fragrances, skin softeners, insect repellents, dyes, vitamins, antimicrobial agents, phase change materials and medical applications (antibiotics, hormones and other drugs).[145]

The encapsulation of compounds, conveys protection towards harmful conditions, from its surroundings, such as, heat, acidity, oxidation, moisture, etc. Additionally, it averts the interaction between the encapsulated with its surrounding, which, in some cases, avoids negative effects. Besides, it allows a controlled and prolonged release of the bioactive principle. Additionally, it may improve chemicals handling, and reduce its exposure to workers or consumers.[145,146] This approach has been broadly explored, over the last years, especially for drug delivery, and in this context, different types of carriers have been investigated, such as liposomes, polymeric nanoparticles, silica nanocapsules, solid lipid nanoparticles, etc.[147–149]

This methodology purposes aim to reduce the amount of antimicrobial applied, for a more cost-efficient utilization of antimicrobial agent. Furthermore, the possibility of negative effects on the end product, such as undesired variations on products properties (due to the interactions of the antimicrobial with the product compounds) or secondary effects on consumers (skin irritation), may be attenuated by using encapsulated antimicrobial compounds relatively to non-encapsulated. Besides, this strategy also enables a more controlled release of bioactive principle. Therefore, encapsulation of antimicrobials has appeared as an alternative to attenuate the aforementioned problematics.[144,147,150,151]

Silica nanostructures have been looked up with interest as a bioactive principles carrier. Its porous structure enables a more controlled release (mesoporous uniform structure), with a tuneable pore size, high surface area, non-toxic nature, etc. A good example of this includes hollow silica nanospheres, which enable a high bioactive principle storage and its controlled release. Recently, the synthesis of silica capsules with PHMB has been demonstrated.[152]

2.4.3. Perfumes

The pleasant odour of a product may play as a powerful motivator towards its purchase. Therefore, perfumed products consist of an approach, which presume the differentiation by manufacturing appealing products to consumer's senses (e.g. perfumed tissue papers). It is noteworthy that human's sense of smell identifies not only the quality of different odours, but, it also associates it (often unconsciously) with feelings ranging

from agreeable to unpleasant. Therefore, perfumed products become more attractive while unpleasant smells are used for the opposite purpose. [153–155]

Many companies have followed this strategy through the years, by developing scent based trademark products.[156] Consumers relish on products carrying a pleasant fragrance. There are plenty examples of perfumed products, ranging from scented letters to washed textile fabrics and so forth. [157] A good well known example are Renova scented facial tissue papers (Figure 2. 26)

Figure 2. 26– Examples of some of Renova scented tissue papers.

Perfumes or fragrances are generally made of volatile compounds collected from a wide variety of plants, grasses, spices, herbs, woods and flowers, such as orange blossoms, jasmine, rose and lavender.[158] Besides natural origin fragrances, there are also those of synthetic origin. All these compounds consist on organic volatile molecules, which are often found on gas or liquid state. These compounds include a panoply of compounds such as alcohols, aldehydes, ketones, esters, acids sulfides, etc. [159]

To manufacture perfumed products, these are often treated with fragrances, typically by spraying, coating or dipping, with a perfume/fragrance. However, the effects of the fragrance on substrates, wears off rapidly. The development of attractive and durable perfumes has been a long-time aspiration of industry. Ergo, research for controlled-release fragrances, as a way to extend fragrance longevity, have been a rather investigated subject during the last decades. Once again, similarly to antimicrobial agents (previous section **2.4.3**.), encapsulation appears as a good way to control fragrance release and turn it more durable. [154,157]

Encapsulation allows an improved performance and stability of perfumes (substantivity, tenacity or endurance), which tends to wear off by evaporation, interactions with other components, oxidation or degradation. Similarly to before (antimicrobials, section **2.4.3.**), by resorting to perfumes encapsulation, it is possible to protect them from surrounding adverse conditions (temperature, pH, water, etc), and therefore achieve a more controlled and longer perfume release. Additionally, it facilitates its handling (e.g. most of the synthetic nitro- and polycyclic musks used in perfumes, are toxic and non-biodegradable), improves its affinity towards the substrate, reduces losses, requires less amounts of perfume, etc.[154,159–161]

Similarly to before, capsules may be produced from various materials, with a variety of shapes (spherical, oblong or irregular, monolithic or aggregates), with single or multiple walls. [154,160] Amongst the most commonly used materials are polysaccharides and sugars (gums, starches, celluloses, cyclodextrin, dextrose, etc), proteins (gelatin, casein, soy protein, etc), lipids (waxes, paraffin oils, fats, etc), inorganics (silicates, clays, calcium sulfate, etc) and synthetics (acrylic polymers, poly(vinylpyrrolidone), etc). [154,159] Although when preparing capsules, it is important to bear in bind its end-use, which is a determining factor for the selection of the most appropriate material. For example, the encapsulation of perfumes in silica nanostructured appear as a rather promising encapsulation method for certain applications. Capsules do not swell or change under pH changes, or temperature variations, alike some many other materials, such as polymers. Other advantages include its inertness, transparency, thermal protection of the active ingredient, protection towards oxidation, it high mechanical resistance, nontoxicity and biocompatibility. Besides enables the encapsulation of both water-based and oil-based liquids.[154,160–162]

2.5. Ultra-high pressure

High pressure processing, also known as high hydrostatic pressure or ultra-high pressure (UHP) has been applied for many years on the production of ceramics, composite materials, plastics and artificial diamond, representing nowadays an expanding technology in food industry. [163–165] Recently this technique was applied for the modification of biopolymers[166–173] and called attention with relation to improve the performance of tissue papers.

2.5.1. Fundaments

Ultra-hydrostatic high pressure technology (UHP) has revealed a substantial growth during the last years, particularly in what concerns food industry, for food processing and preservation, due to the advantages it reveals relatively to other thermal processes. [163]

This technology uses elevated pressure conditions (100-1000 MPa), which are transmitted through a fluid, often water. The technology is based on 3 main principles, *Le Chatlier* principle, the isostatic principles and the microscopic ordering principle. *Le Chatelier* principle[174], states that any phenomena in equilibrium (chemical reaction, phase transition, etc) accompanied by a disturbance tends to counter it. So, in case of a pressure increase, any phenomenon (e.g., chemical reactions, phase transitions or changes in the molecular configuration) which is accompanied by a decrease in volume is enhanced and vice-versa. Since many biochemical reactions include volume variations, therefore

biological processes are affected by pressure. UHP mainly affects non-covalent bonds such as hydrogen, electrostatic, etc, meaning that low molecular weight components are normally less affected whereas high molecules components are more sensitive to UHP.[168,175,176]

The isostatic principle,[168,175] is also present on this technology and it implies that pressure is applied instantaneous and uniformly, regardless of the samples dimensions (in case of solid samples their format remains intact). This particularity constitutes a huge benefit, as concerns heat treatments (such as thermal pasteurization), since temperature treatments do not allow a uniformly distribution of temperature, generating temperature gradients, and due to the high temperatures samples are subjected, it may affect thermosensitive compounds. [168,175,176]

Finally, the microscopic ordering principle[168,175] states that upon constant temperature an increase in pressure increases the degrees of ordering of molecules of a given substance.

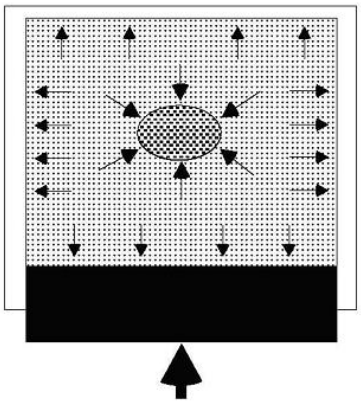

Figure 2. 27 – Schematic representation of the isostatic principle.[176]

2.5.2. UHP applications and effects

UHP may be found in many applications, in food industry and for biotechnological applications, its major effects include (i) microorganisms inactivation, (ii) biopolymers modification (protein denaturation, protein activation/deactivation, gel formation, etc (iii) ability to retain food products quality, specially colour and flavour (since UHP mainly affects non-covalent bonds) and (iv) effects on products functionality (changes on density and texture).[177] However, only biopolymer modification by UHP will be given focus, since corresponds to the essence of current work.

As mentioned above UHP treatment is able to induce changes on structural and functional level of biomolecules, and example of this would be enzymes denaturation or starch gelatinization. [163–168,170–173,176,178–184] Additionally, more recently, changes in cellulose structure, have also been demonstrated.[169,185,186]

Studies performed by Figueiredo *et al*[169] with kraft and sulfite pulps under pressure condition of 400MPa, demonstrated structural changes in cellulose. It was demonstrated that during UHP treatment the crystallites average width in fibrils increases, as result from partial cocristalization of crystalline regions on adjacent elementary fibrils, when favourably orientated and free of noncellulosic compounds. Additionally, it was also revealed that UHP induces forced hydration on amorphous regions enabling an improving of fibres swelling abilities, and thus decreasing the hornification effect affecting them. Moreover, treated fibres became more flexible and elastic rendering improved mechanical properties. Due to forced hydration on amorphous and crystalline regions, fibrils became less aggregated and thus more accessible towards chemical reactants, namely diluted sulfuric acid.[169]

The improved accessibility of cellulose pre-treated with UHP, was also demonstrated as regards enzymes.[185,186] This was demonstrated when treating *E. globulus* kraft pulp with cellulase and xylanase (Figure 2. 28). In these studies, it was verified that UHP pre-treatment, similarly to before, induced forced hydration, and therefore rearrangements that promoted fibril disaggregation and thus higher accessibility towards sites previously inaccessible. Owing to these facts the accessibility of enzymes towards cellulose was higher and therefore higher rate and degrees of hydrolysis were achieved. [185,186]

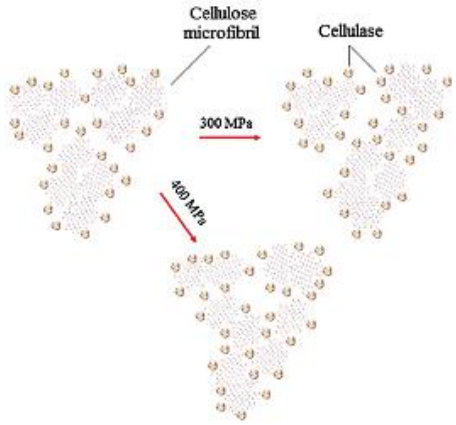

Figure 2. 28 – Schematic representation of UHP effect on cellulosic fibres accessibility towards cellulases.[185]

Figure 2. 29 – Images of two of hydrostatic high pressure equipments owned by the University of Aveiro. On the left is the Hyperbaric 55 with a 55 L capacity and on the right is the High-pressure U33 with a capacity of 100mL.

It is yet to discover the effect of UHP on other types of fibres, specially recycled fibres, which are highly affected by hornification. This constitutes a rather curious topic since papermaking industry feedstock is not solely based on *E. globulus* pulps. Besides the effect of high pressure towards other types of chemical/reactants commonly used on papermaking industry also poses and intriguing topic as concerns fibres modification and its process efficiency.

2.6. References

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Chapter III

Effect of ultra-high pressure on cellulosic fibres structure

Contents

3.1. Introduction

With nowadays environmental issues, recycling is recognized as a path towards a more sustainable future. A good example is paper recycling. Its benefits are not only economical, but also environmental.[1] Although attractive, materials recycling still pose a few drawbacks, such as the number of times recycling is possible due to materials degradation. [1,2] In the case of paper recycling, the use of recycled pulp still exhibits disadvantages relatively to virgin fibres, which are essentially related to (i) feedstock variability, (ii) losses on fibres mechanical/physical properties, (iii) hornification, (iv) and impurities.[1–5]

Overall authors agree that the main responsible for recycled pulp properties loss is the hornification effect. The hornification effect occurs mostly due to the formation of irreversible hydrogen bonds, between fibrils, yielding fibril aggregation, fibre collapse, stiffening, inability to swell as originally and hence losses on mechanical and hydration properties. [2,6,7] These structural changes occur mostly due to successive swelling, pressing, drying, printing, storing, re-dispersing and deinking processes. [2,3,7–10]

The inability of fibres to swell like originally represents a rather relevant matter, since by becoming stiff and less malleable, these features are transmitted to its end products. Besides, the stress fibres are subjected during their life cycles further intensifies the hornification effect, leading towards a continuous loss on fibres properties. [6–10]

The aptitude of fibres for hornification depends on different variables, such as the wood origin, the pulping method, fibres biometry, storage conditions and chemical composition.[6,7] For example, it has been demonstrated that hornification affects easier low yield pulps relatively to high yield pulp. This difference is related to a higher lignin and hemicellulose content, such as the case of high yield pulps, which act as a barrier against the formation of irreversible hydrogen bond formation between fibrils.[2,6,7]

Although impurities also affect fibres properties hornification is still considered the major responsible for the losses felt on the recycled fibres properties. [2,11] In pulp and paper industry these losses are considered a major issue, since they comprise a hindrance not only for manufacture but also as regards the end-products features. To surpass these issues methods have been developed, through time, as a way to diminish the negative effects brought by hornification on fibres. These methods include beating, chemical treatment with alkaline solutions, mixture with virgin fibres, fibres fractionation and more recently enzymatic treatment. [2,3,7–10]

In tissue paper industry besides recycled fibres, virgin fibres are also extensively used for the production of tissue paper. Being pulps absorbency (hydration abilities), softness and its capacity to maintain integrity (mechanical properties) considered as the most important features on tissue paper, with special emphasis on absorbency.[12,13] Fibres ability to interact with water molecules (facial tissue) and became softer, or its ability to absorb vast amounts of water (kitchen paper towels), is essential to tissue paper industry. To evaluate materials hydration different methods may be followed, such as moisture sorption isotherms, capillary rise tests, contact angle analysis, etc. There are numerous tests, which enable the evaluation of a fibres ability to interact with water, which could be seen an indirect measurement of pulp accessibility towards OH groups, as mentioned in the previous chapter.

Ultra-High pressure (UHP) emerges here as a non-degrading alternative technology with the ability to decrease hornification on fibres and improve its accessibility. The potential of UHP on cellulosic pulps has been demonstrated in literature, as concerns *E. globulus* kraft pulp and sulfite pulps, and is fully described in the previous chapter. It has been shown that UHP induces structural rearrangements on cellulosic fibres, rendering improved accessibility and reduced hornification to cellulosic fibres. [14–16]

However, there is still much to explore as concerns the use of UHP treatment for the modification of recycled fibres, which are highly affected by hornification and which behaviour under UHP conditions is unknown. With these in mind, the main purpose of the work displayed on this chapter was to evaluate the effect of UHP on recycled and different virgin fibres (hardwood and softwood fibres). Additionally, changes in its properties were evaluated, with special emphasis on its hydration properties and its ability to introduce strongly bound water. All this allowed the evaluation, for the first time, of the hydration behaviour of recycled fibres.

3.2. Materials and Methods

Different cellulosic pulps were provided by Renova. Premium recycled fibres (alpha-recycled fibres), ***R***, produced by Renova from paper wastes, collected in 30.10.2012 was supplied for the studies. Additionally, bleached *Eucalyptus Globulus* industrial *kraft* pulp (purchased to Portucel Soporcel group, lot 35I-179025), ***E***, was also supplied along with bleached softwood pulp (purchased to Botnia group, lot 4B21263), ***S***, for comparative reasons.

3.2.1. Chemical characterization

When received all cellulosic pulps were analysed according to its moisture content, ash content, intrinsic viscosity, carbonyl and carboxyl contents and sugar composition.

3.2.1.1. Moisture content

The moisture content from 1g of pulp was determined on an oven at 105ºC following norm TAPPI T 412 om-11.

3.2.1.2. Ash content

Following procedure **3.2.1.1**, the ash content was also determined at 525±25ºC, in agreement with norm Tappi T 211 om-07.

3.2.1.3. Extractives

- Acetone (99.9%, HPLC grade, Acros Organics)

The extractives content, in pulp samples, was determined considering norm Tappi T204 om-88, using acetone as solvent.

3.2.1.4. Intrinsic viscosity

- Cupper-ethylenediamine solution (CED, Panreac)
- Distilled water

Intrinsic viscosity was determined by dissolution of pulp samples in CED (cupper-ethylenediamine) solution, according to norm SCAN-CM 15:88.

3.2.1.5. Carbonyl content

- Chloride of 2,3,5-trifenil-2H-tetrazolium (98%, Sigma-Aldrich)
- KOH (87%, Acros Organics)
- Ethanol (99%, Acros Organics)
- Glucose (99%, Sigma-Aldrich)

- Distilled water

The carbonyl content was determined following procedures from literature.[17,18] The method is based on the ability of these groups to reduce the chloride of 2,3,5-trifenil-2H-tetrazolium (TTC), yielding a compound of red colour called formazan (Figure 3. 1), which is easily identified and quantified by UV-Vis spectroscopy. This method is known as the Sabolks method.

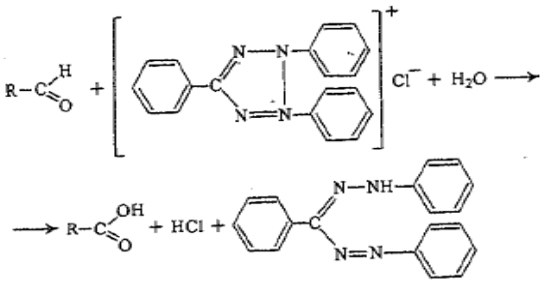


Figure 3. 1 – Reaction between TTC and carbonyl groups from cellulose.

For this test a solution A (0.2 M of KOH), a solution B (0.2% (w/w)) of TTC in ethanol, glucose, a porous glass filter and a volumetric tube (10 mL) are required.

Initially, 0.010 g (+0.0001 g) of each sample was weighted into a Soviril tube (5mL). Later 0.5 mL of solution A was added followed by 0.5 mL of solution B. The tube was then closed and placed in boiling water for 2 min. Subsequently to the reaction, pulp should exhibit a red coloured complexion. Afterwards, the tube was placed on ice to cool down. The tube content was then filtered with a glass filter, with vacuum, as represented in Figure 3. 2

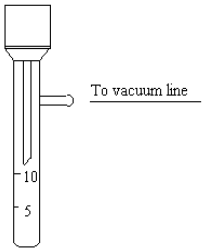


Figure 3. 2 – Image of the volumetric tube equipped with a glass filter used on the procedure.

Pulp still with red colour was washed with ethanol, continuously until the red colour vanished. This operation was performed with a glass rod and ethanol was added for washing until the filtrate on the tube made a total volume of 10 mL. The solution was then analysed by UV-Vis spectroscopy on a UV-mini-1240 apparatus from Shimadzu, at 546 nm using a 10 mm cell. At the same time, a blank experiment was also carried out, with a similar procedure, but without pulp. The blank was used as reference for all measurements.

i) Calibration curve

The concentration of aldehyde groups was determined considering a calibration curve made with glucose as standard. To do so, a glucose solution was prepared (0.1% (w/w)) and 10, 25, 40 and 50 μL of this solution was placed on 4 tubes. Then, to each tube, 0.5 mL of Solution A and 0.5 mL of solution B were added. The mixture was then placed in boiling water for 2 min. Afterwards, each tube was cooled down on ice and ethanol was, then, added until the total volume reached 10 mL. Finally, each solution was analysed by UV-Vis spectroscopy, in the same way as before. The calibration curve at the end related absorbance with C=O weight (mg).

Considering the mass of carbonyls determined through the calibration curve, the content of carbonyls was determined for each sample according to Equation 3.1, where M correspond to C=O mass (mg) considering the calibration curve, and G is the mass of pulp weighted.

$$C = O\left(\frac{mmol}{100g\ of\ pulp}\right) = \frac{M \times 100}{G \times 28{,}018} \qquad \text{Equation 3. 1}$$

3.2.1.6. Carboxyl content

- HCl (37%, Acros Organic)
- NaCl (99%, Sigma-Aldrich)
- $NaHCO_3$(97%, Fluka)
- Distilled water

The amount of carboxyls was determined following an adaptation of norm T237 om-93. To do so, 2±0.1 g of pulp was weighted and placed into a 500 mL erlenmeyer (in duplicate). Then 250 mL of HCl 0.1 M were added and the suspension was left stirring for 4h, to insure that all carboxyl groups were in its protonated form. Afterwards, the pulp was filtered and washed with water until the filtrate pH matched water pH.

The filtered pulp was weighted and added to 500 mL of $NaHCO_3$ and NaCl solution (prepared by dissolving 0.84 g of $NaHCO_3$ and 5.85 g de NaCl in 1 L of H_2O). This dispersion was then left stirring during, at least, 12 h. Afterwards, the pulp was filtered again under vacuum, while the filtrate was collected in a dry buchner flask. Two aliquots of this liquid were collected, 20 mL each, and placed into 100 mL erlenmeyers. To prepare a blank test, 20 mL of the $NaHCO_3$ and NaCl solution was pipetted into a 100 mL erlenmeyer.

The solution alkalinity was determined by titration with HCl 0.01 M with methyl red. The amount of carboxyls in 100 g of dry pulp was determined according to Equation 3.2,

where *a* is the volume (mL) of 0.01 M HCl spent on titration, *b*, is the volume (mL) of 0.01 M HCl spent on the blank titration, *G* is the weight (g) of water in pulp after the titration, and *w* is the weight of the dry pulp (g).

$$COOH\left(\frac{mmol}{100g}\right) = \left(b - a - \frac{G \times a}{50}\right) \times \left(\frac{50}{25 \times w}\right) \qquad \text{Equation 3. 2}$$

3.2.1.7. Neutral sugar analysis

- H_2SO_4 (96%, Acros Organics)
- NH_3 (25%, Panreac)
- 2-desoxiglucose (99%, Acros Organics)
- $NaBH_4$ (99%, Acros Organics)
- Glacial acetic acid (99.7%, Fluka)
- 1-methylimidazol (99%, Sigma-Aldrich)
- Acetic Anhydride (99%, Acros Organics)
- Acetone (99.9%, HPLC grade, Acros Organics)
- Distilled water

In order to determine the neutral sugar content, on each sample, the procedure followed three reaction steps, hydrolysis, reduction and acetylation.[19]

i) Hydrolysis

The first step consisted on the samples hydrolysis. With that in mind, 10 mg of pulp were weighted into a soviril tube (in duplicate). Into each tube, 400 µL of H_2SO_4 (72%) were added, followed by 3 h incubation at room temperature. Afterwards, 4.4 mL of distilled water were added and the tubes were left to incubate at 100ºC for 2h30. Later the tubes were placed on ice to cool down.

ii) Reduction

The next step consisted on the reduction of sugars resultant from the hydrolysis step. To do so 200 µL of 2-desoxiglucose (10 mg/mL) were added as internal standard, to each tube. Then 1 mL from this mixture was placed in a new tube, to which 0.2 mL of NH_3 (25%) and 0.1 mL of NH_3 (3 M) containing 150 mg/mL de $NaBH_4$, were further added (while the tubes are still kept on ice).

Samples were then left to incubate under 30 ºC during 1 h. Afterwards, all tubes were placed again on ice, to cool down. To each tube, 50 µL of glacial acetic acid was added, twice, followed by agitation, in order to destroy the excess of $NaBH_4$.

iii) Acetylation

The last reaction step consisted on the acetylation of the sugars reduced in the previous step. To do so, 0.3 mL from each tube was poured into new tubes, followed by the addition of 0.45 mL of 1-metthylhimidazol and 3 mL de acetic anhydride. Subsequently, the tubes were left to incubate for 30 min at 30 ºC and later placed on ice to cool down.

When cooled down, 3.75 mL of distilled water (water excess to destroy the acetic anhydride) and 2.5 mL of dichloromethane (extraction of the alditol acetates) were added. The mixture was agitated with a vortex apparatus and when phase separation was verified, with a Pasteur pipette, the upper layer of liquid (aqueous phase) was removed. Then 3 mL of distilled water and 2 mL of dichloromethane were added and mixed again with the vortex apparatus. When phase separation was verified the upper layer liquid layer was removed again (aqueous phase). The same procedure was repeated three times but without the dichloromethane addition. After this procedure, the tubes content was placed under nitrogen flow for evaporation and, when dried, to the residue inside the tubes 1 mL of acetone was added. Then samples were once more placed under nitrogen flow for evaporation. This evaporation procedure was repeated one more time.

iv) Gas chromatography analysis

The residue resultant from the previous stage was dissolved in 100 µL of dry acetone and 1 µL of the resultant mixture was injected into a chromatographer Focus GC from Thermo Scientific, with a Restek Corp column, RTX-225 (L=30 m; id=0.25 mm and df=0.25 µm) and FID detector, under the following conditions: injector temperature at 225 ºC, column temperature at 220 ºC e detector temperature at 250 ºC.

The calibration curves determined for each standard were determined and are represented in Appendice A.

3.2.1.8. Acid methanolysis for analysis of monosaccharides and uronic acids

- NaCl (99%, Sigma-Aldrich)
- H_2SO_4 (96%, Acros Organics)
- Methanol anhydrous (99,9% HPLC grade, Acros Organics)
- Sorbitol (98%, Sigma-Aldrich)
- Pyridine (99%, Acros Organics)
- Hexamethyldisiloxane (99%, Acros Organics)
- Trimethylchlorosilane (99,5%, Sigma-Aldrich)

The acid methanolysis procedure was performed with HCl anhydrous (in methanol). In order to prepare this reactant 75 g of NaCl were weighted and placed into a double neck round glass flask. The main entry of this flask was meant for concentrated H_2SO_4, while the other worked as an exit for the gas produced during the reaction (HCl). This output was linked into a recipient, on ice, containing dry methanol (50 mL), followed by a second recipient containing NaOH for neutralization of the residual HCl gases. The final solution of methanol and HCl was titrated to access the molar content of HCl, which was determined to be 1.8 M.

After preparing the main reactant, the methanolysis procedure took place according to reference[20]. To do so, 4.5 mg of fibres were weighted and placed on a soviril tube, to which 2 mL of HCl (in methanol) were then added. Each sample was tested in duplicate. Afterwards, each tube was left to incubate for 4 h during 100 ºC.Then to each tube 80 μL of pyridine and 1 mL of standard sorbitol solution 0.1 mg/mL (prepared with methanol) was added to each tube). From each tube, 2 mL of the mixture was then removed, placed on new tubes, and evaporated with N_2. To the remaining dry residue 70 μL of Pyridine, 150 μL of hexamethyldisiloxane and 80 μL de trimethylchlorosilane were added. After 12 h at room temperature, the samples were analysed by GC-MS. The samples were analysed by a gas chromatographer Trace Gas Chromatograph 2000 series, equipped with a mass detector from Thermo Scientific DSQII, using helium as carrier gas (35 cm/s). The chromatographic conditions were as follows: column capillary DB-1J&W (30 m x 0.32 mm i.d.0.25 lm); initial temperature of the column 100 to 4 ºC/min 175 ºC following by 175–12 C/min; final temperature 290 ºC, and detector temperature 290 ºC.

3.2.1.9. Determination of residual lignin and hexuronic acids amount

- Cadmium oxide (99.5%, Sigma-Aldrich)
- Ethylenediamine (99%, Sigma-Aldrich)
- Distilled water

The residual lignin content and the amount of hexuronic groups (HexA) were determined according with literature[3], through UV-Vis spectroscopic analysis of samples dissolved in cadoxen. Cadoxen was prepared from ethylenediamine (EDA) aqueous solution and cadmium oxide, following the same reference.[21]

Cadoxen is a solvent capable of dissolving pulp, with properties favourable to UV-Vis spectroscopy, such as the absence of a visible band and transparency in the UV region.

When dissolved on cadoxen, polysaccharides exhibit great stability to oxidative degradation, enabling thus the storage of such solutions for a long periods of time. These advantages allow the quantification of lignin through UV spectroscopy, at 280 nm, on bleached and non-bleached pulp, dissolved in cadoxen. Cadoxen itself exhibits an absorption and below 220 nm. However, the UV region above 220 nm can still be considered for analysis.

Between 230 and 350 nm, it is possible to identify the contribution of residual lignin and hexuronic groups from xylans. The absorption at 231nm is attributed to the hexenuronic groups. In the case of residual lignin this last exhibits an absorption band at 280 nm, a shoulder between 240-255 nm and some absorption at 230 nm.

Considering this the absorptions at 231nm and 280 nm of pulp solution in cadoxen can be expressed by Equations 3.3 and 3.4, where ε_{231}^{HexA}, ε_{231}^{Lig}, ε_{280}^{HexA} e ε_{280}^{Lig} are the absorptivity's of the hexuronic groups (HexA) and of residual lignin (Lig), at its characteristic wavelengths 231nm and 280 nm. The concentrations (g/L) of HexA and Lig are given by C_{HexA} and C_{Lig}, respectively.

$$A_{231} = \varepsilon_{231}^{HexA} \cdot C_{HexA} + \varepsilon_{231}^{Lig} \cdot C_{Lig} \qquad \text{Equation 3. 3}$$

$$A_{280} = \varepsilon_{280}^{HexA} \cdot C_{HexA} + \varepsilon_{280}^{Lig} \cdot C_{Lig} \qquad \text{Equation 3. 4}$$

Considering the abovementioned equations, the concentrations of HexA (g/L) and Lig (g/L) can be determined by Equations 3.5 and 3.6.

$$C_{Lig}\left({}^{g}/_{L}\right) = \frac{A_{280}\cdot {\varepsilon_{231}}^{Hex} - A_{231}\cdot {\varepsilon_{280}}^{Hex}}{{\varepsilon_{231}}^{Hex}\cdot {\varepsilon_{280}}^{Lig} - {\varepsilon_{231}}^{Lig}\cdot {\varepsilon_{280}}^{Hex}} \qquad \text{Equation 3. 5}$$

$$C_{HexA}\left({}^{g}/_{L}\right) = \frac{A_{231}\cdot {\varepsilon_{280}}^{Lig} - A_{280}\cdot {\varepsilon_{231}}^{Lig}}{{\varepsilon_{231}}^{Hex}\cdot {\varepsilon_{280}}^{Lig} - {\varepsilon_{231}}^{Lig}\cdot {\varepsilon_{280}}^{Hex}} \qquad \text{Equation 3. 6}$$

To determine the amount of residual lignin and the amount of hexuronic acids, the procedure was carried out as described below. Air dried pulp, with known moisture content, was weighted, 25 mg, and placed on a 50 mL erlenmeyer for dissolution with 15 mL of cadoxen. The procedure was performed in duplicate. All solutions were then left stirring for1-3 h until pulp dissolution. Then 15 mL of distilled water was added to each Erlenmeyer, and the mixture was left homogenizing for 10-15 min. All solutions were then filtered with a glass porous filter and analysed by UV-Vis spectroscopy, on Jasco V 560 UV–VIS spectrophotometer.

All spectra were recorded considering as reference a solution 1:1 water:cadoxen, on a quartz cell with 10 mm dimensions, between 200 nm and 500 nm. The concentrations of

residual lignin and hexuronic acids were determined considering values from literature given by Table 3. 1.

Table 3. 1– Absorption coefficients of residual Lignin and HexA.[3]

	Absorption coefficients	
	ε_{280} (L.g^{-1}.cm^{-1})	ε_{231}(L.g^{-1}.cm^{-1})
HexA residue	3.8	31.8
Residual Lignin on *E.globulus* pulp	17.3	34.0
Residual Lignin on softwood pulp	18.6	39.0

Afterwards, the amount of hexuronic acids (mmol/Kg) and the percentage of residual lignin were determined according to Equations 3.7 and 3.8, where C_{HexA} and C_{Lig} represent the HexA and the Lignin concentration (g/L) in solution and *G* represents the mass of pulp weighted.

$$HexA\ (mmol/kg) = \frac{C_{HexA} \cdot 30ml \cdot 1000}{G \cdot 176g/mol} \qquad \text{Equation 3. 7}$$

$$Lig\ (\%) = \frac{C_{Lig} \cdot 30}{G \cdot 10} \qquad \text{Equation 3. 8}$$

3.2.2. Hydrostatic ultra-high pressure treatment (UHP)

- Propylene glycol (96%, Dowcal)
- Distilled water

To perform the hydrostatic ultra-high pressure treatment (UHP) pulp samples were dispersed in distilled water with 2% consistency and placed in sealed containers. The samples were subjected to 400 MPa, during 15 min, at 20 ºC, in a High-pressure U33 equipment, with a 100 cm^3 capacity, with propylene glycol:water (1:1) as transmission medium.

After the treatment, the samples intended for the preparation of handsheets for analysis were stored, while the samples meant for other tests were filtered, air dried and stored in a plastic bag.

3.2.3. Preparation of standard handsheets for analysis

Pulp dispersions prepared according to Renova procedure norm PT.Lab.106 were prepared and used to produce standard handsheets following ISO 5269-2:2004, on a Rapid-Köthen (Karl Schröder KG) sheet former. The same was performed using the dispersions treated with UHP from section **3.2.2.**

3.2.4. X-ray diffraction (XRD)

Samples with and without HP were subjected to x-ray diffraction, in a Philips X'Pert diffractometer, equipped with a Cu$K\alpha$ (λ=0.154 nm) monochromatic radiation source.

To become possible, the analysis of pulp samples, pellets of each sample were prepared. With that in mind, 100 mg of each pulp were weighted and a 5 ton pressure was applied to each sample with a press. All pellets were analysed between 4 and 40 º of 2θ(º) at 0.02 º/scan. The determinations of the parameters, D_{200}, b and of the crystallinity degrees, for each sample, were performed in agreement with literature methods.[16,22]

3.2.5. ^{13}C solid state NMR

Structural changes on pulp samples were also followed by ^{13}C solid state Cross Polarization-Magic Resonance (^{13}C CPMAS NMR). The spectra were registered on a Bruker Avance 400 spectrometer. Samples were packed into a zirconia's rotor sealed with Kel-FTM caps and spun at 9 kHz. Acquisition parameters were as follows: ca 7000 scans with a 90 proton pulse, a cross-polarization contact time of 1 ms and a recovery delay of 2.5 s. The determination of the crystallinity indexes were performed considering the methods form literature.[16,23]

3.2.6. Fourier transform infrared spectroscopy (FTIR)

- D_2O (99.8%, Acros organics)
- KBR (99+%, Acros Organics)
- P_2O_5 (98%, Acros Organics)

Changes in fibres structure were also monitored by FTIR of deuterated samples. With that in mind, a set of two replicas from each sample were prepared. Initially, both replicas were dispersed under deuterated water, although while replica one was subjected to HP treatment (400 MPa, 15 min), replica two remained under D_2O for 15 min (the same amount of time required for the UHP treatment). It is noteworthy that both replicas were initially dispersed with the sample consistency (2%) on D_2O. Afterwards, all pulp samples were filtered, allowed to hydrogenate under room conditions, then placed at 105 ºC to achieve complete dryness and then stored in a desiccator under P_2O_5. Pellets with pulp and KBR were then prepared, from each sample, (2 mg of pulp: 250 mg of KBR) for analysis on a Bruker optics tensor 27, with 128 scans and with 4cm^{-1} of resolution. FTIR spectres were normalized an approximately at 2900 cm^{-1}, which corresponds to the C-H stretching vibration band.

3.2.7. Scanning electron microscopy (SEM)

Pulp samples were analysed through scanning electron microscopy (SEM), on a Hitachi S4100 equipment at 15 kV. Each sample was attached to a SEM support with carbon tape and then subjected to Au/Pd sputtering before analysis.

3.2.8. Capillary rise

Capillary rise tests were performed according to ISO 8787:1986, which is based on the Klemm Method.

3.2.9. Contact angle analysis

- Formamide (Acros Organics, 99%)
- Diiodomethane (Acros Organics, 99%)
- Distilled water

Contact angle analysis was performed on the standard handsheets prepared in 3.2.3., on a Surface Energy Evaluation System equipment from *dataphysics*, through the *sessile* drop method, considering three different liquids, water, formamide and diiodomethane.

The polar and dispersive component from the surface free energy was determined for each sample according to the Owen-Wendt method[24], using the data collected from the contact angle from each liquid in each sample.

3.2.10. Texture analyses

The texture from each handsheet sample was also analysed through microtopographic analysis, performed on an *Altisurf 500* profilometer. The scanned area was 4.8x4.8 mm^2 with 2 μm of resolution. For each sample, four acquisitions were obtained in different sites.

3.2.11. Zeta Potential

Variations on the pulp samples charge were also followed by zeta potential measurements, on pulp dispersions diluted with distilled water. Complementarily, each solution pH was also measured using a pH Meter, model HI2020 - edge® multiparameter, from Hanna Instruments. Zeta potential measurements took place on a *Malvern Zeta Sizer Nano Series*, apparatus using disposable plastic cells.

3.2.12. Moisture sorption isotherms (gravimetric method)

- KOH (87%, Acros Organics)
- LiCl (99%, Acros)
- CH_3COOK (99,+%, Acros Organics)
- $MgCl_2 \cdot 6H_2O$ (99%, Acros Organics)
- K_2CO_3 (99%, Alfa Aesar)
- $Mg(NO_3)_2$ (99%, Acros Organics)
- KI (99,+% Acros Organics)
- $(NH_4)_2SO_4$ (99%, Carlo Erba).

Moisture sorption isotherms determination followed a static gravimetric method, at 25, 30 and 35ºC, in a wide range of relative humidity values (0-100%), using different saturated salt solutions to insure so.[25]

Beforehand, pulp samples (1g) were left drying on a desiccator (with P_2O_5), in nylon bags, to ensure complete dryness. When completely dried, samples were attached to the top of closed flasks containing saturated salt solutions, and then placed in a water bath (Jubalo SW23) with controlled temperature. All samples were weighted periodically until equilibrium was reached (approximately 7 days).

The experimental data were then fitted to GAB (Guggenheim, Anderson and de Boer) model. The nonlinear regression analysis of the experimental data was performed using Matlab r2012a curve fitting tool. The adequacy of the fitting was evaluated according to the coefficient of determination (R^2) and RMSE (root mean squared error), devolved by Matlab.

3.2.13. Calorimetric analysis

The calorimetric analysis was performed on a thermally isolated container with a thermometer with 0.01 ºC accuracy. Water was weighted (200 g) and placed on the calorimeter for a blank experiment. Afterwards, 2 g of absolutely dried pulp (previously dried over P_2O_5 in a desiccator), was placed on the calorimeter and changes on the system temperature were followed through the thermometer. The difference of temperature attained during the experiment was corrected with a blank experiment (only water) and then, the heat released during the wetting process of cellulosic fibres was determined considering the equations 3.9-3.11

$$Q_w = m_w \times c_w \times \Delta T \qquad \text{Equation 3. 9}$$

$$Q_w = Q_p \qquad \text{Equation 3. 10}$$

$$Integral\ heat\ of\ wetting = \frac{Q_p}{m_p} \qquad \text{Equation 3. 11}$$

Where Q_w (J) is the heat absorbed by water, m_w the mass (g) of water, c_w, the specific heat capacity of water ($J.g^{-1}.{}^oC^{-1}$), ΔT the difference of temperature measured between the beginning and end of the experiment (ºC), and Q_p the heat released by the fibres during the wetting process, (J).

3.2.14. Thermal analysis

Samples, previously saturated at 100 HR%, at room temperature, were subjected to thermogravimetric analysis, TGA, which was performed in a *Setsys Evolution 1750* apparatus, from *Setaram* from 30 to 700 ºC at 10 ºC/min. Additionally, differential scanning calorimetry, DSC, was also performed, on a *Power Compensation Diamond DSC* equipment from *PerkinElmer* from 30 to 180 ºC at 10 ºC/min.

3.3. Results and Discussion

3.3.1. Pulps characterization

Cellulosic pulps supplied by Renova, namely recycled fibres, ***R***, bleached kraft *E. globulus* pulp, ***E***, and softwood pulp, ***S***, were received and analysed for its composition and other general parameters. The results achieved are presented in Table 3. 2 and 3. 3, respectively.

Pulps composition was accessed according to its sugar composition from its hemicelluloses. Recycled fibres, ***R***, displayed a composition similar to that of hardwood pulps, with high amounts of glucose and xylose, although very small amount of galactose and mannose were also detected. These residual sugar content could be easily explained by variabilities on the feedstock used to produce recycled pulp, which consisted, mainly, of hardwood pulp products (e.g. office papers), along with residues of softwood pulp products.

As regards ***E***, this displayed a typical composition of *E. globulus* hardwood pulp, as described in the literature, with a high amount of glucose and xylose, due to the presence of glucuronoxylans (the most abundant hemicelluloses on this type of wood).[26] Whereas ***S*** exhibited a high content of glucose accompanied by a lower xylose content, with monosaccharides such as mannose, galactose and arabinose, typical from softwood pulps.[26] The second method (methanolysis) for sugar analysis, relatively to the first, enables the determination, exclusively, of hemicelluloses including uronic acid residues, which is not possible through the first method. For example, in the case of 4-*O*-Me-GlcA, this compound is easily found on hardwood pulps (*O*-Acetyl-4-*O*-methylglucuronoxylans, typical hardwood xylan).

Table 3. 2 – Composition of neutral sugars %(w/w) of ***R***, ***E*** and ***S*** cellulosic pulps.

	R % (w/w)	E % (w/w)	S % (w/w)		R % (w/w)	E % (w/w)	S % (w/w)
Neutral Sugars analysis by Saeman hydrolysis				**Monosaccharides and uronic acids by methanolysis**			
Glc	78.8±2.2	75.4±2.3	85.1±1.5	Glc	43.8±1.1	34.7±0.4	50.6±1.7
Xyl	17.7±2.3	24.6±2.5	9.2±1.4	Xyl	43.5±2.4	62.6±0.2	26.0±1.4
Ara	0.5±0.1	Trace	0.7±0.1	Ara	0.6±0.3	0.0±0.0	1.5±0.07
Man	2.8±0.1	Trace	4.9±0.7	GalA	0.3±0.03	0.4±0.08	0.08±0.04
Gal	0.2±0.1	Trace	0.1±0.04	4-*O*-Me-GlcA	0.8±0.08	0.8±0.04	0.0±0.0
				Gal	9.8±0.9	0.8±0.05	20.9±0.19
				Man	1.2±0.05	0.7±0.08	0.9±0.09

Other general parameters were also investigated such as the ash content, intrinsic viscosity, extractives, residual lignin, hexenuronic acids, carbonyls and carboxyls content, and these results are displayed in Table 3. 3.

Table 3. 3- Results of chemical analysis of ***R***, ***E*** and ***S***.

	R	E	S
Ash content (%)	1.83±0.05	0.14±0.02	0.07±0.04
Extractives (in acetone) (%)	0.15±0.01	0.24±0.02	0.13±0.01
Intrinsic viscosity (mL/g)	540±10	925±1.0	610±5.0
Carbonyls (mmol/100g pulp)	1.26±0.07	0.76±0.03	0.97±0.1
Carboxyls (mmol/100g pulp)	7.0±0.1	6.80±0.3	4.0±0.3
Residual Lignin (%)	-	0.11±0.01	0.18±0.01
Hexenuronic acids (mmol/kg)	-	5.2±0.02	10.0±0.02

Recycled fibres, ***R***, exhibited a high amount of ash, which is agreement with the presence of inorganic impurities, such as fillers. These results are indicative that recycled fibres still possess impurities (acquired during its life cycle) that were not possible to remove completely, even after the purification process.[2] On the other hand, virgin pulps (***E*** and ***S***), as expected from bleached virgin pulps, exhibited a low ash content, which is atributed to the multiple washing stages they were subjected during its production.[27,28]

The intrinsic viscosity parameter was also evaluated. In the case of ***R***, the registered low intrinsic viscosity suggests fibre degradation (cellulose depolymerization during fibres life cycle).[2] At the same time, virgin fibres (***E*** and ***S***) exhibited typical values.[27] Although in the case of ***S***, viscosity could be affected by a severe pulping process, thus producing lower polymerization degrees, which affected intrinsic viscosity. [27]

The carbonyl content displayed the highest value for ***R***, suggesting the eventual presence of chromophore structures in recycled fibres, most likely due to organic impurities or due to the fibres ageing.[2] On the other hand, ***E*** and ***S*** exhibited a lower carbonyl content, which is in agreement with virgin bleached pulps.

Residual lignin and hexenuronic acids (HexA) content were also determined.[21] Results were achieved for both virgin pulp, ***E*** and ***S***, however, for ***R*** the same was not possible by this method. A possible explanation would be the interference of ***R*** impurities on the procedure, which relies on spectroscopic analysis of cadoxen-dissolved pulp.

The determined values registered a similar and low residual lignin content in the studied pulps. In addition, ***S*** exhibited a higher amount of HexA than ***E***. This difference could be attributed to a harsher cooking procedure suffered by ***S***, when compared to ***E***, and a predominant TCF bleaching of ***S*** pulp.[27,28]

3.3.2. Structural changes upon UHP treatment

Samples ***R***, ***E*** and ***S***, were subjected to UHP treatment at 400 MPa during 15 min. These conditions were selected based on work previously performed.[14–16] For simplicity, each sample treated with UHP will be labelled as ***RHP***, ***EHP***, and ***SHP***, respectively.

Structural changes induced by UHP on fibres were followed by various techniques, such as XRD, NMR, FTIR of deuterated samples, zeta potential and SEM analysis. Additionally, the effects of UHP treatment on pulps hydration abilities were also accessed through capillary rise tests, contact angle analysis (a measure of wettability), moisture sorption isotherms and calorimetric analysis along with thermal analysis (TGA/DSC).

3.3.2.1. XRD and NMR

Structural changes on cellulosic fibres were accessed through XRD and ^{13}C RMN, both on UHP treated and non-treated pulp samples. XRD data enabled the determination of the crystallinity degree (*CD*), and unit cell parameters, D_{200} (average crystallite width from plane 200) and *b* (average height of cellulosic crystalline cell). Table 3. 4 display the results achieved for all UHP treated (***RHP***, ***EHP*** and ***SHP***) and non-treated samples (***R***, ***E*** and ***S***). When comparing treated with non-treated samples, overall UHP samples revealed a higher average crystallite size, D_{200}, up to ca. 16%. Besides, its *CD* also exhibited an increase, when comparing with non-treated samples, with exception of the pair ***S*** and ***SHP***.

These changes mentioned above, have already been demonstrated previously, [16] where it was showed that UHP treatment induces rearrangements on cellulosic fibres structure were suggested, leading towards the convergence of conveniently orientated crystallites, and thus larger crystallites (co-crystallization). Moreover, the rearrangements induced by UHP also could produce chain rearrangements on paracrystalline regions yielding, more crystalline material on the surface, and thus higher *CD*.[16]

Table 3. 4 – Cellulose parameters obtained by XRD analysis.

Samples	$2\theta_{002}$ (º)	$2\theta_{040}$ (º)	D_{002} (nm)	b (nm)	CD (%)
R	22.5	34.5	4.5	1.03	70.9
RHP	22.5	34.6	5.2	1.03	71.5
E	22.5	34.6	5.0	1.03	71.1
EHP	22.5	34.6	5.6	1.03	71.7
S	22.6	34.6	6.0	1.03	75.2
SHP	22.6	34.6	6.3	1.03	74.7

Table 3. 5 – Crystallinity index determined by ^{13}C NMR.

Sample	^{13}C NMR, Crystallinity index (%)
R	46.5
RHP	48.2
E	45.4
EHP	46.0
S	50.5
SHP	51.0

Changes in fibres structure were also followed by ^{13}C solid-state NMR (Appendices B). The data obtained was used to determine the crystallinity index of each sample. This parameter was determined considering the ratio between the area of ordered ($A_{86ppm-92ppm}$) and amorphous ($A_{79-86ppm}$) regions.[23] These results are presented in Table 3. 5 and from the results obtained, it was possible to observe that UHP treated samples revealed higher crystallinity index when compared with non-treated samples. These results further support XRD results, as concerns the changes suffered by fibres on its crystalline regions,[16] and allows to confirm the possibility of method error in case of XRD data, for samples pair ***S*** and ***SHP***. Additionally, the presented results suggest that ***R***, ***E*** and ***S***, upon UHP treatment, exhibit similar behaviour not differing much from each other.

3.3.2.2. FTIR of deuterated samples

Structural changes on fibres along with the presence of strongly bound water, as result of UHP treatment, were investigated by FTIR of pulp samples subjected to H/D exchange with heavy water, in liquid phase, as described in section **3.2.6.** The spectra of samples were normalized according to 2900cm^{-1} band (C–H stretching vibration) and are represented in Figures 3.3 and 3.4.

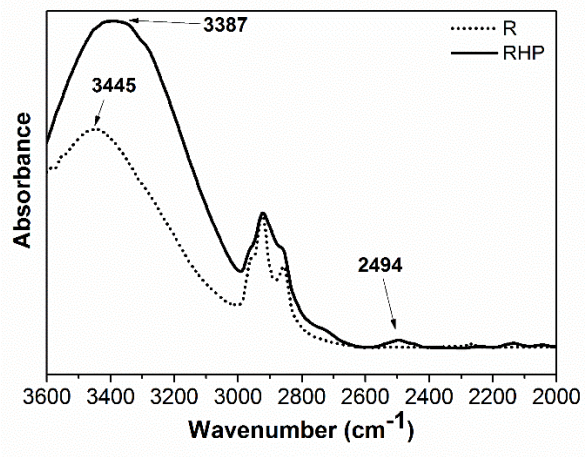
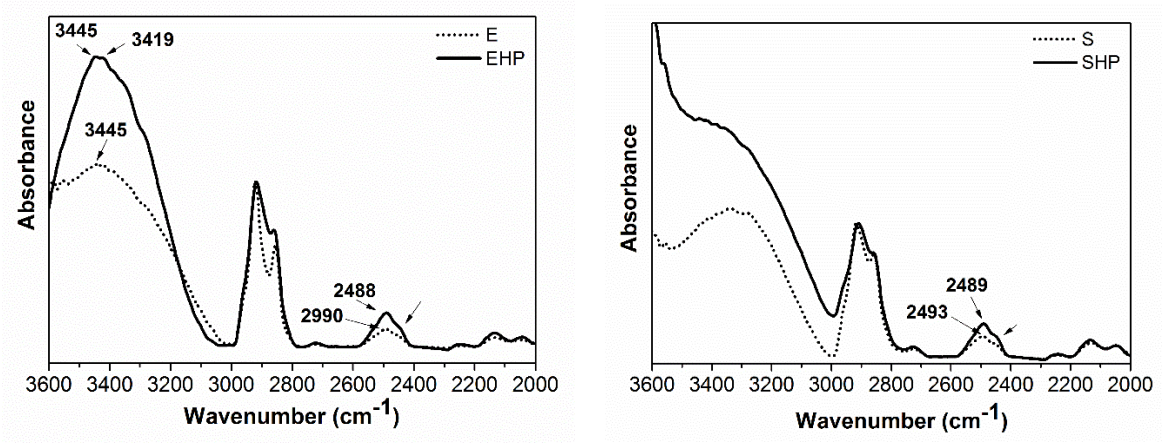


Figure 3. 3- Normalized FTIR spectra of deuterated samples ***R*** and ***RHP***.



(a) (b)

Figure 3. 4 – Normalized FTIR of deuterated samples ***E*** and ***EHP***, a); and ***S*** with ***SHP*** b).

The spectra of recycled fibres, with and without UHP, (***RHP*** and ***R***, respectively) in Figure 3. 3, display the typical OD band[29–31] at 2494cm^{-1}for ***RHP***, while ***R*** did not show this band. The presence of absorbance at approximately 2500cm^{-1} in ***RHP*** spectra suggests that either OD groups were not able to perform the exchange from OD to OH, due to structural changes, or, considering the effects induced by UHP (structural rearrangements, increased accessibility, forced hydration, etc).[16] D_2O entered deep inside the fibre structure, into previously inaccessible sites, remaining imprisoned under the form of strongly bound water (not leaving even at 105ºC). Additionally, the OH band shift from 3445cm^{-1} to 3387cm^{-1}, into smaller wavelengths, also suggests thus, since it entails more intensive OH bonds.

As regards virgin fibres FTIR spectra showed some different results (Figure 3. 4). Upon UHP, hardwood (***EHP***) and softwood fibres (***SHP***), both revealed an intense peak at 2488cm^{-1}and at 2489 cm^{-1}, respectively (OD band). These peaks were accompanied by shoulders at smaller wavelengths. Nevertheless, ***E*** and ***S***, in opposite to recycled fibres, exhibited a smaller, but still well detectable, peak at ca 2940 cm^{-1} and 2943cm^{-1}, respectively (even after drying of non-pressurized pulps). Although, it is noteworthy that the OD peak intensity of ***EHP*** and ***SHP*** was much more expressive than that on ***RHP***.

Since recycled fibres (hornified fibres) exhibit a collapsed structure, lower macroporosity and hindered accessibility, the penetration of D_2O on these fibres is probably more difficult than on virgin fibres (less collapsed structure with higher macroporosity). Therefore, it is possible that these facts contribute for the higher D_2O penetration and retention on virgin fibres, comparatively to recycled ones, even upon UHP.

The fact that virgin UHP untreated pulps still exhibited a visible OD band, could be explained by irreversible changes suffered by virgin fibres during the drying process,

which hindered the H/D exchange (resistant OD). Hence, it is possible that the same was not observed for recycled fibres, ***R***, for the above mentioned reasons (hornified fibres with low porosity). It is also noteworthy that, deuteration in most cases is not completely reversible if structural alterations take place on virgin fibres, due to drying (hornification), the exchange from deuterium to hydrogen becomes more unlikely.[29–32] Moreover, the shift observed from ***R*** to ***RHP***, on the OH band, suggests the possibility of shorter distance and more intensive interactions between polymer molecules and water (forced hydration), after the UHP treatment. The hypothesis of water imprisonment by UHP treatment and other of its effects is on a scheme presented in Figure 3. 5.

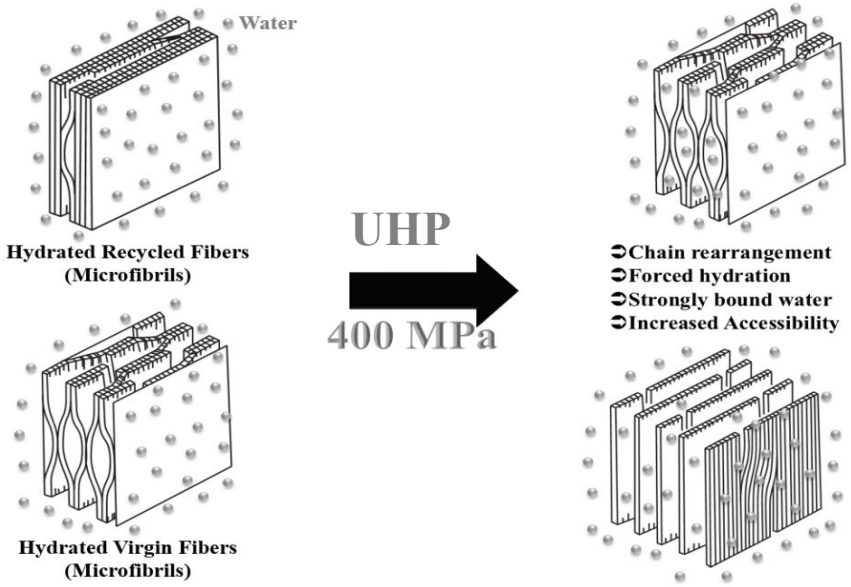


Figure 3. 5– Schematic representation of the phenomena behind UHP treatment (adaptated from *Scallan* microfibril drying scheme [11,33,34]).

3.3.2.3. Zeta Potential

The effects induced by UHP on fibres were further analysed by zeta potential measurements (Table 3. 6). As expected for cellulosic material all samples exhibited negative charges.[35] This occurs because when a charged surface is immersed in a solution containing ions, an electrical double layer is formed (Figure 3. 6). In the case of cellulose (negatively charged), the sources behind its charge could be related with the dissociation of ionic groups on the particle surface (e.g. COOH groups of cellulose). The negatively charged surface (Figure 3. 6) attracts oppositely charged ions (counter-ions) and repels ions of the same charge (co-ions). If it were possible to separate the two-phase, they would carry equals and opposite charges.[35]

Cellulose is negatively charged throughout a wide pH window and depending on the cellulose origin its zeta potential approaches zero between 4-5.[36,37] The ionisable groups

on cellulosic fibres may be carboxyl groups, hemiacetal, sulfonic acid groups, phenolic groups among some others. Under normal papermaking conditions, the carboxyl and sulfonic acid groups are the major contributors to fibre charge. Most of the carboxyl groups originate, either from non-cellulosic components in wood itself or are created during the pulping and bleaching operations. Sulfonic acid groups are introduced with sulfite treatment during CTMP or chemical pulping.[35]

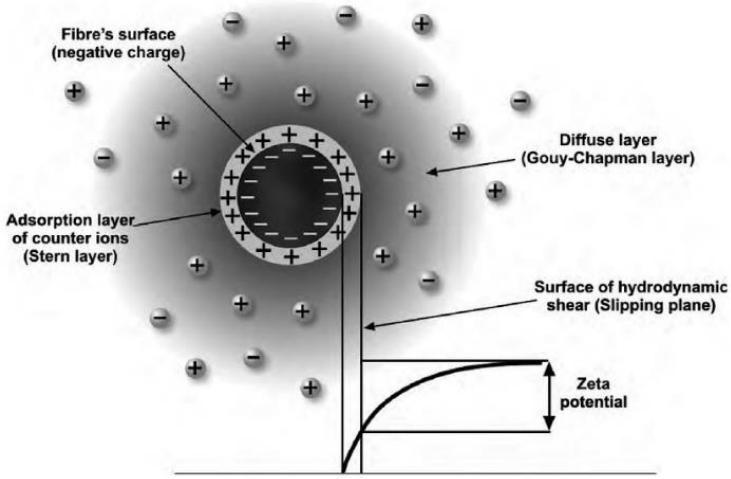


Figure 3. 6 – The electrostatic double layer on the surface of a material.[38]

Although negatively charged, UHP treated samples exhibited lower negative zeta potential charges than untreated ones. These results suggested the diminishing of surface potential (Ψ_0) or the increasing of the Stern layer. As cellulosic pulp was not subjected to a radical chemical or physical modification with a drastic change of its structure, the changes in Ψ_0 are very unlikely. Most likely, the forced hydration led to the diminishing of the surface conductivity of cellulose material, due to the delocalization of its negative charge, thus increasing the Stern layer.

From a papermaking point of view, the decrease of pulps zeta potential, upon UHP treatment, could be considered a positive point, since it may contribute, for example, to decrease the demand on retention aids to facilitate paper formation.

Table 3. 6– Zeta potential measurement and its pHs values, of pulp samples treated with and without UHP.

Sample	Zeta potential (mV)	pH
R	-19.5±7.2	5.55
RHP	-2.5±4.4	5.53
E	-15.4±3.5	5.93
EHP	-9.9±5.6	5.69
S	-30.1±6.8	5.61
SHP	-20.4±5.9	5.63

3.3.2.4. SEM

The morphology of UHP treated (***RHP***, ***EHP*** and ***SHP***) and non-treated (***R***, ***E*** and ***S***) samples was also accessed through scanning electron microscopy (SEM). Recycled fibres are represented in Figure 3. 7 (***R*** and ***RHP***), while virgin fibres images are represented in Figure 3. 8 (***E*** and ***EHP***), and in Figure 3. 9 (for ***S*** and ***SHP***). Overall, it was possible to observe, on the surface of treated fibres, an increase on surface irregularity. It was suggested that macrofibrils upon UHP "swelled", standing out more than before. These gains in bulk and surface roughness are in agreement with fibril disaggregation and forced hydration, especially, forced hydration. Similar features have been observed for cellulosic fibres, in literature, using a optic microscopic imaging. [16] Therefore it explains the bulkiness gained by macrofibrils, and thus its higher exposure on the surface.

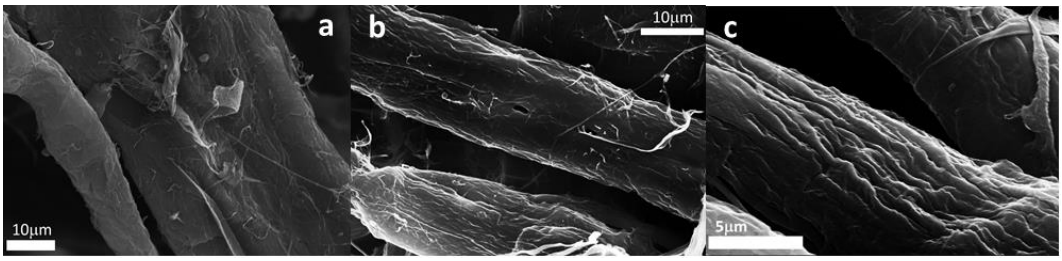


Figure 3. 7- SEM images of ***R*** (a) and ***RHP*** (b and c).

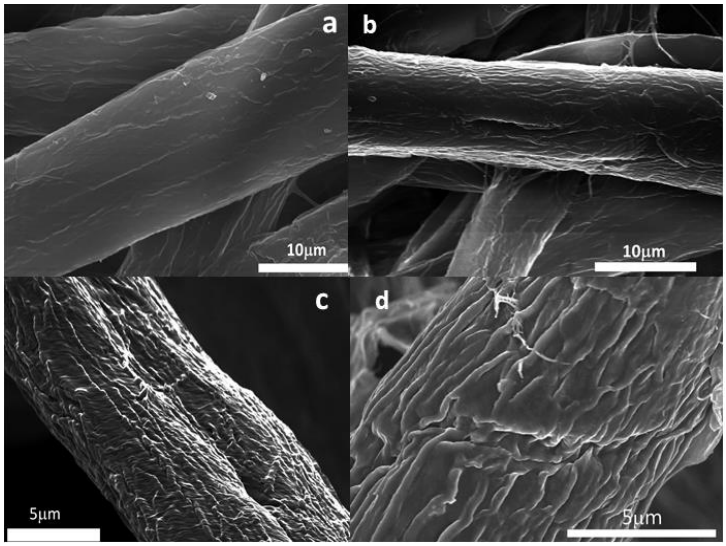


Figure 3. 8-SEM images of ***E*** (a) and ***EHP*** (b,c and d).

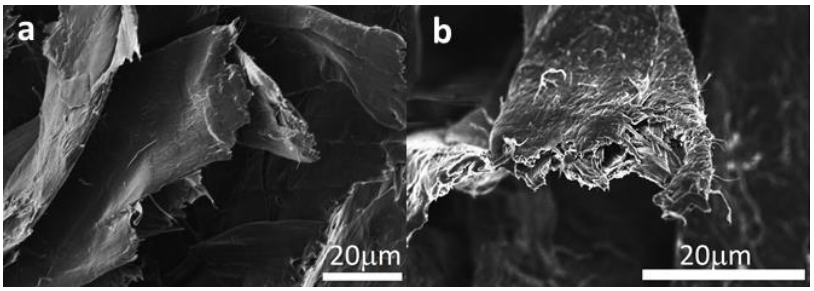


Figure 3. 9– SEM images of ***S*** (a) and ***SHP*** (b).

3.3.3. Interactions between fibres and water upon UHP treatment

The affinity between fibres and water plays a key role in tissue paper industry. Therefore, this point was of special attention in order to better comprehend how UHP affects fibres. This was critical for recycled fibres due to their hard hornification. With this in mind, water affinity in samples, with and without UHP treatment, were investigated, regarding its affinity towards water using capillary rise tests, contact angle measurements, moisture sorption isotherms, thermal and calorimetric analyses.

3.3.3.1. Capillary rise tests

The contribution of UHP towards fibres affinity to water uptake was investigated by capillary rise tests and its results are displayed in Table 3. 7. It was found that upon UHP (***RHP***, ***EHP***, ***SHP***), samples revealed higher capillary rise when compared with non-treated samples (***R***, ***E***, ***S***). Recycled fibres registered an increase of ca. 11% from ***R*** to ***RHP***, while virgin fibres displayed an increase of ca. 3.5 % from ***E*** to ***EHP***, and of 19% from ***S*** to ***SHP***. These findings evidenced that UHP promoted fibres accessibility towards water due to the fibril disaggregation and thus contributed to the decrease of hornification,[15,16] negatively affecting recycled fibres. These effects originated not only from extra free OH groups (previously unavailable) but also from a less collapsed structure of cellulosic fibres and improved macroporous structure in pulp sheets, i.e. for an easier ascension of water molecules through fibres.

The UHP treatment effects were particularly strong on recycled fibres (***R*** and ***RHP***) and on softwood virgin fibres (***S*** and ***SHP***). In the case of recycled fibres due to hornification, its structure is collapsed, with low porosity and poor accessibility to free OH groups. Upon UHP treatment, the rearrangements and fibril disaggregation provoked by this treatment, originate improved accessibility to inner fibre layers and to more free OH groups. Since recycled fibres display more limited hydration skill, due to the aforementioned reasons, this may explain why its results were better than those of its homologous, hardwood pulp. In the case of softwood fibres (***S*** and ***SHP***), these were the ones displaying the highest increase in the capillary rise. Although being "dried" virgin fibres, it is possible that its structure, in terms of porosity and accessibility to OH groups, were somehow jeopardized. This may be true if during its production harsh conditions were used. Therefore, although being "virgin fibres" its full potential is not available. As result, upon UHP treatment, it is possible that UHP reversed the aforementioned limitations enabling a substantial improvement of softwood fibres capillarity.

Table 3. 7– Capillary rise of UHP treated (***RHP***, ***EHP*** and ***SHP***) and non-treated samples (***R***, ***E*** and ***S***).

Sample	Time (min)	Capillary rise (mm)
R	10	49.5 ± 0.25
RHP	10	55.0 ± 0.25
E	10	125.5 ± 0.25
EHP	10	130.0 ± 0.50
S	10	105.5 ± 0.25
SHP	10	125.5 ± 0.70

3.3.3.2. Contact angle analysis

Cellulosic fibres wettability was also investigated by contact angle (CA) measurements, with different liquids of known contribution of polar and apolar energy (water, formamide and diiodomethane). These tests have been performed from cuts of handsheets prepared from each sample. CA results were also corrected (Table 3. 8) considering the surface roughness of samples (Table 3. 9), using the Wenzel equation. [39–41]

As regards recycled fibres, samples treated with UHP (***RHP***) revealed a slight increase of CA with water, when compared with untreated samples, which is indicative of a slight decrease on wettability. From CA results, surface free energy was also determined, according to Owen-Wendt relationship.[24] The obtained results showed a small decrease of the surface free energy, from untreated to UHP-treated recycled fibres (from ***R*** to ***RHP***), with slight variations on its polar (decrease) and dispersive (increase) contributions. It is possible that this slight decrease on hydrophilicity could be related with a redistribution of hydrophobic impurities in recycled fibres, during UHP treatment. However, the small variations registered and its deviations (between non-treated and UHP-treated samples), suggest that further studies, with other techniques, are required to evaluate more correctly the effect of UHP treatment on recycled fibres hydrophilicity.

In the case of hardwood virgin fibres, CA with water decreased, in samples subjected to UHP treatment (ca. 10% from ***E*** to ***EHP***). This result is indicative of an improvement on the handsheets wettability.[42] Additionally, the surface energy results revealed an increase in samples treated with UHP, comparatively to untreated samples, with variations on its polar (increase) and dispersive (decrease) contributions. The increase in the surface energy, especially of its polar contribution, confirms the improvement of this pulp hydrophilicity, after the UHP treatment. This fact may be related to the increased amount of free OH groups in pulps that appeared with the disaggregation of fibrils. Besides, fibres

macroporosity also plays an important role. Thus, it is possible that the capacity of UHP to improve porosity also contributes to an improved wettability.

Similar to recycled fibres, softwood virgin fibres also revealed ambiguous results, with no significant variations of CA and of its surface energy and its respective contributions. It is possible that the type of fibres (softwood, long fibres) is responsible for the different impact of UHP treatment on fibres, comparatively to hardwood virgin fibres (short fibres). However, further studies with other techniques are required to scrutinize the effect of UHP treatment on the hydrophilicity of softwood virgin fibres.

Table 3. 8– Contact angle (CA) and surface energy values for treated (***RHP***, ***EHP*** and ***SHP***) and untreated pulps (***R***, ***E*** and ***S***).

Sample	Contact angle (º)*			Surface energy (mJ/m^2)	Polar (mJ/m^2)	Dispersive (mJ/m^2)
	Water	Formamide	Diiodomethane			
R	54.4±1.1	51.1±0.3	66.5±0.9	45.1±4.3	30.7±2.5	14.4±1.7
RHP	58.7±1.3	49.9±0.9	60.7±1.4	42.5±3.7	24.1±2.0	18.4±1.7
E	65.2±1.5	47.7±0.8	63.7±1.3	39.0±5.6	19.2±2.8	19.8±2.8
EHP	58.8±1.3	53.7±0.9	62.2±1.2	41.7±5.9	24.8±3.3	16.9±2.7
S	58.3±1.1	51.0±0.7	61.9±1.0	42.5±4.0	25.0±2.2	17.5±1.8
SHP	59.2±1.3	50.1±1.5	64.0±1.8	42.0±3.1	24.9±1.7	17.1±1.4

*All contact angles were corrected according to Wenzel equation [39–41].

Table 3. 9– Surface texture parameters from handsheets prepared from ***R***, ***RHP***, ***E***, ***EHP***, ***S*** and ***SHP***.

Sample	Average roughness(μm)	*Sdr* (%)
R	4.1±0.1	23.8±2.0
RHP	4.5±0.03	29.5±0.6
E	4.4±0.05	38.4±0.6
EHP	4.6±0.1	40.9±2.0
S	5.4±0.2	34.5±2.6
SHP	5.9±0.2	41.5±1.7

**Sdr* (developed interfacial area ratio, % of surface area increase by the contribution of texture comparatively to plane surface) *Sdr*= 0: plane surface; *Sdr* ≠0: surface with texture (> *Sdr* → surface with more texture).

Table 3.9 shows that samples prepared from fibres subjected to UHP treatment (***RHP***, ***EHP*** and ***SHP***) exhibited higher roughness, comparatively to untreated fibres.

The wetting behaviour of materials is governed by both their chemical composition and its geometric surface structure. Accordingly, an increase in roughness, on a hydrophobic/hydrophilic surface, results in more interfacial area, for interaction between surface and liquid. Therefore increasing roughness may originate a material more hydrophobic/hydrophilic.[39,43] In the case of the three pulps under study, when pre-treated

with UHP, the roughness of the handsheets prepared was higher, comparatively to those prepared from untreated pulps. However, only hardwood virgin fibres revealed a rather significant variation on wettability. Hardwood virgin fibres (from ***E*** to ***EHP***) hydrophilicity and the increase in roughness may explain the decrease of CA with water and the variations in surface energy. However, the same may not be valid for softwood virgin fibres and recycled fibres. Hence, it is noteworthy the necessity of complementary tests to scrutinize more correctly fibres hydration behaviour upon UHP.

3.3.3.3. Moisture sorption isotherms

Moisture sorption isotherms are widely used to evaluate materials hydration mechanisms. With this in mind, this method was employed to investigate the changes resulting from UHP treatment on cellulosic fibres. Thus, samples treated (***RHP***, ***EHP*** and ***SHP***) and not treated by UHP (***R***, ***E*** and ***S***) were scrutinized for its moisture sorption isotherms at 25, 30 and 35 ºC. The results achieved are represented in Figures 3.10 and 3.11.

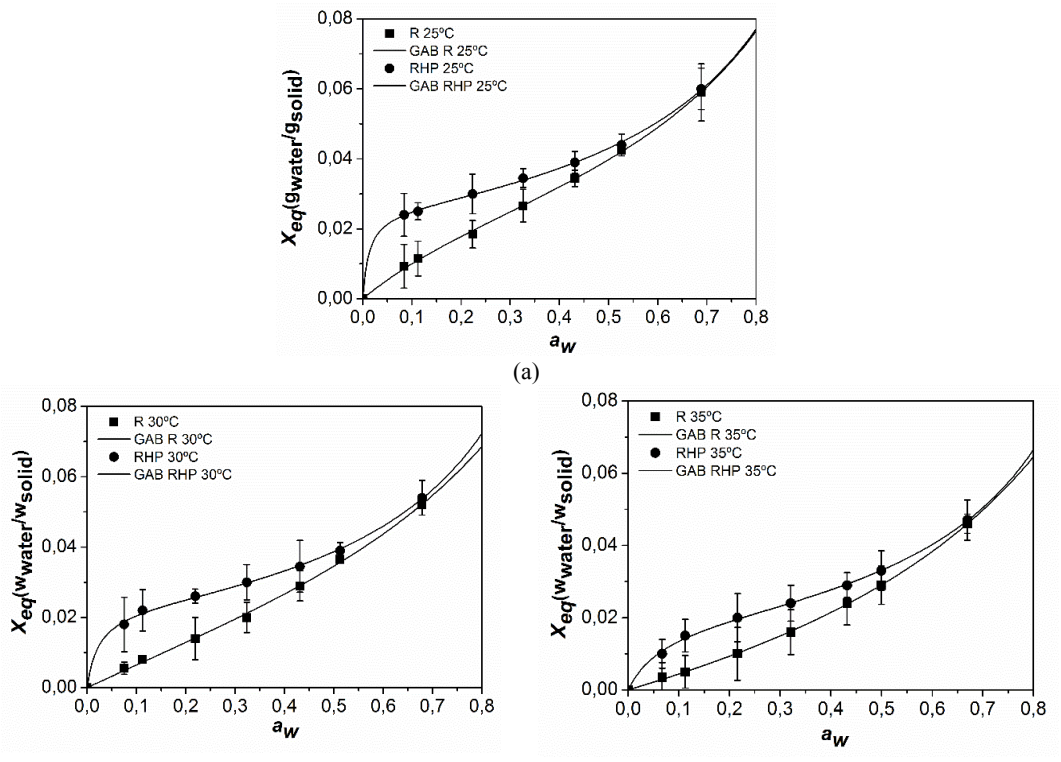


Figure 3. 10 - Moisture sorption isotherms at 25, 30 and 35 ºC for recycled fibres treated (***RHP***) and non-treated (***R***) by UHP.

The moisture sorption isotherms determined for ***R*** and ***RHP*** evidenced a rather significant difference, from each other, in the studied temperature range. The changes were quite evident, since ***RHP*** exhibited improved moisture sorption, describing a pattern closer to that of virgin fibres (type II isotherm according with *de Brunauer* classification[44]), with

monolayer formation. In opposite, ***R*** exhibited a quite limited moisture uptake, as consequence of hornification, with insignificant monolayer formation (at all studied temperatures). In contrast to ***RHP***, ***R*** behaviour was much similar to that of a type III isotherm, typical for hydrophobic materials.[45]

The sorption isotherm changes found from ***R*** to ***RHP*** can be explained by the effects, previously discussed, induced by UHP treatment. UHP enabled structural rearrangements, at fibrils level (i.e. decrease of fibril aggregation and pore/fibres collapse), which contributed to a significant increase of accessible surface with free OH groups. As a consequence, the limitations on water sorption by hornified recycled fibres decreased substantially, after the UHP treatment.[14–16]

Even though recycled fibres (***R***) are known to be highly hornified, damaged, contaminated with impurities, and possibly with chemical modifications[2], hornification is still considered the main responsible for its limited accessibility to free OH groups and thus its limited water sorption. Nevertheless, the already mentioned effects, induced by UHP, contributed significantly to improve recycled fibres water sorption, which for tissue paper consists in a rather relevant issue.

In the case of virgin fibres (***E, EHP, S***, and ***SHP***, Figure 3. 11), when compared to recycled ones (***R*** and ***RHP***) a different trend in water sorption was observed. Although virgin fibres described the typical type II isotherm behaviour [45,46], when treated with UHP (***EHP*** and ***SHP***), a small decrease in its moisture sorption capacity, X_{eq}, was registered, at all studied temperatures.

In virgin fibres, the fibrils aggregation is much less expressed than in recycled fibres. Hence, the decrease found could be related to the effect of forced hydration, i.e. the presence of significant amounts of strongly bound water, enough to diminish free OH groups and hinder water molecules absorption to form the monolayer. It has been demonstrated[16] before, and confirmed by results of the present study, that UHP is able to decrease aggregation, improve accessibility and to introduce strongly bound water in fibres. It may be proposed two competing processes upon UHP treatment of pulp. One is related to the appearance of new accessible cellulosic surface free OH, due to fibrils disaggregation and another is the formation of cellulosic clathrate hydrates (Figure 3. 12), where part of free OH groups is involved in strong interactions with water (less free OH). In the case of virgin fibres, with relatively high accessible surface, the second process is predominating, whereas, for recycled fibres, the first one is the most important. This proposition is supported by the results of H/D exchange on virgin and recycled pulps.

Thus, the amount of strongly bound D_2O in virgin pulps was much superior than in recycled pulps (Figures 3.3 and 3.4)

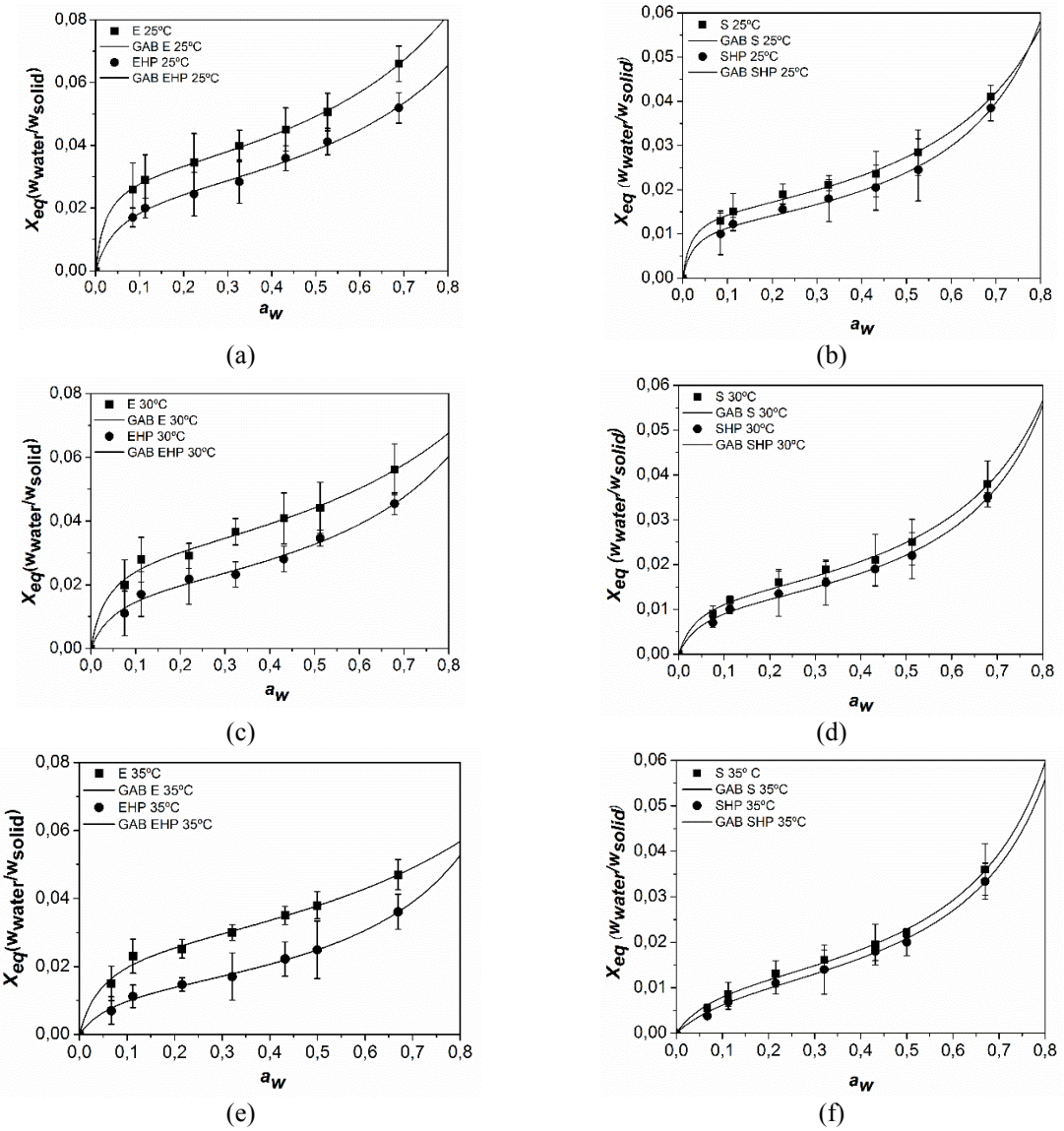


Figure 3. 11- Moisture sorption isotherms at 25, 30 and 35 ºC for virgin pulps treated with UHP (***EHP*** and ***SHP***) and non-treated (***E*** and ***S***).

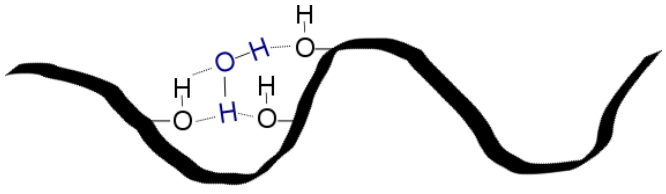


Figure 3. 12 – Illustration of a possible clathrate hydrate formation. Free OH groups are involved in strong hydrogen bonding with water becoming "frozen".

The experimental data was also fitted considering models with physical meaning, widely employed in the study of these type of systems, such as BET and GAB models. However, here will only be considered GAB model, which is less limiting, more versatile

and widely used with positive results describing moisture sorption on cellulosic materials.[45,46]

The fittings were performed on Matlab2012a, on its curve fitting tool. The adequacy of the fitting was evaluated considering the values devolved by Matlab of R^2 (coefficient of determination) and RMSE (root mean squared error). GAB parameters were determined by non-linear regression analysis. The sorbents specific area was also determined in agreement with Equation 2.2 from ***Chapter 2***, section **2.1.6.1**. The results achieved are given in Table 3. 10 - 3.12.

GAB parameters were estimated and analysed for ***R*** and ***RHP*** (Figure 3. 10). The estimated monolayer, X_m, for ***R*** displayed quite high values, which do not agree with the observable pattern followed by the isotherm, with no significant monolayer. The fact that GAB model estimated a rather high value for the monolayer, suggests that the model was not able to predict this parameter correctly. It is noteworthy that the aforementioned model is mostly used to describe type II isotherms (with monolayer formation), which may explain its difficulty estimating a more accurate value.

Table 3. 10 - Fitting and GAB parameters achieved from ***R*** and ***RHP*** non-linear regression, with confidence intervals of 95%.

Parameters	R			RHP		
	GAB (25ºC)	GAB (30ºC)	GAB (35ºC)	GAB (25ºC)	GAB (30ºC)	GAB (35ºC)
R^2	0.9992	0.9986	0.9997	0.9994	0.9998	0.990
RMSE	6.5E-4	7.8E-4	3.1E-4	5.1E-4	6.2E-4	5.5E-4
C	4.7±1.32	2.3±1.5	1.3±0.9	94.9±54.4	50.4±23.8	16.6±4.7
X_m	0.0322±0.007	0.0407±0.03	0.0466±0.04	0.0253±0.001	0.0226±0.002	0.0199±0.002
k	0.7830±0.1	0.6975±0.2	0.6925±0.2	0.8431±0.03	0.8633±0.04	0.8865±0.05
S(m^2/g)	134.62	170.167	194.9	105.6	94.4	83.0
ΔH_c (kJ/mol)		98.3			133.1	
ΔH_k (kJ/mol)		9.4			-3.8	
C_0		2.8E-17			4.9E-22	
k_0		2.0E-2			3.95	
$\Delta H_{s,t}$(kJ/mol)		88.9			136.9	

Nevertheless, in the case of ***RHP***, since it behaves as a type II isotherm, with monolayer formation, a more correct estimate of the monolayer was possible. It also revealed, as expected, a decreasing monolayer with temperature.[47,48] The monolayer formation on ***RHP*** is a sign of the decrease on fibres hornification (more free OH groups for the formation of the first layer of water molecules). The specific surface area was also determined, however, a comparison between ***R*** and ***RHP*** was not possible, due to its direct dependence with X_m, which was despised due the aforementioned reasons.

Parameter *C* and *k* were also estimated. While the first parameter is related to the strength of binding in the monolayer, the other is indicative of the organization of the multilayer.[49] The values determined for *C*, as expected, decreased on both ***R*** and ***RHP*** with temperature. However, when comparing ***R*** with ***RHP*** values an increase was found, which is in agreement with the formation of the monolayer in ***RHP***. The formation of the monolayer led to intensive interactions between cellulose free OH groups with water, corresponding to a higher enthalpy of hydration.

The estimates of parameter *k* displayed a decrease in ***R***, and an increase for ***RHP***, with increasing temperature. This parameter correlates water molecules properties from multilayer and bulk water. As *k* approaches 1, little is the distinction between multilayer molecules and liquid ones. In the case of ***R*** sample, due to its lacking of free OH groups to form the monolayer, the multilayer gains increasing significance and thus its contribution plays a bigger role on water sorption, comparatively to the monolayer, with increasing temperature. On the other hand, since RHP is able to form a monolayer, in terms of water sorption, with increasing temperature, the multilayer loses importance. Its values increase towards one suggest that the properties of the water molecules multilayer tend to those of bulk water, with increasing temperature.[49]

When comparing the values of *k* for ***R*** and ***RHP***, it was observed that the values from the first were lower than those estimated for the second. This suggests that in ***RHP***, the contribution of the multilayer for water sorption is less significant, as previously mentioned, due to the formation of the monolayer, where more intensive interactions between cellulose and water molecules have a higher contribution.

From the temperature dependence of parameters *C* and *k*, it was also possible to determine C_0, k_0 and ΔH_c and ΔH_k (Equations 2.3 and 2.4 from ***Chapter 2***, section **2.1.6.1.)**. Parameters C_0 and k_0 are entropic in nature and, similarly to *C* and *k*, one is related with the monolayer, while the other is related with the multilayer. C_0 values are expected to be smaller than 1 (molecules prefer the multilayer than the monolayer from an entropic point of view), while k_0 values are expected to be higher than 1 (high entropy of molecules in liquid water).[49] As expected, C_0 displayed very small values, which became even smaller on UHP treated samples (***RHP***), due to the formation of the monolayer. Also, k_0, which was lower than 1, for samples treated with UHP, became higher than 1, possibly due to the higher entropy existing between water molecules. As discussed before, these results are in agreement with a higher accessibility to OH groups and a higher water uptake, due to UHP.

The estimates of ΔH_c and ΔH_k (enthalpy of the monolayer formation and multilayer, respectively)[49], were determined. It was found from non-treated (***R***) to UHP treated samples (***RHP***), an increase on ΔH_c (from 98.3 to 133.1 kJ/mol) and a decrease on ΔH_k (from 9.4 to -3.8kJ/mL). The ΔH_c results are in agreement with the formation of a monolayer in ***RHP***, as discussed previously. Since a higher amount of water molecules are bound to the surface in the monolayer, a higher solvation enthalpy was registered. Furthermore, the decrease found on ΔH_k, is also indicative of the decrease in importance of the multilayer. As previously discussed, it is possible that with the formation of a more composed first layer of molecules at the surface (monolayer of ***RHP***), the water molecules in the multilayer interact less intensively (in ***RHP*** comparatively to ***R***), which requires less enthalpy to remove the multilayer molecules.

From the values of ΔH_c and ΔH_k (Equation 2.7, ***Chapter 2***, section **2.1.6.1.**), it was also possible to estimate the net isosteric heat of sorption ($\Delta H_{s,t}$), which were 88.9 kJ/mol and 136.9 kJ/mol, respectively for ***R*** and ***RHP***. The substantial increase found from the first to the latter, further supports UHP as a regenerative treatment, able to decrease the limitation imputed by hornification on fibres hydration abilities.

For comparison, the moisture sorption isotherms of virgin fibres (***E***, ***S***, ***EHP*** and ***SHP***) were also fitted according to GAB model. The fitting results are displayed in Table 3. 11 and 3. 12. From both tables, it is possible to observe that GAB described well all isotherms as displayed by the high values of R^2 (near 1) and low RMSE values.

Table 3. 11 – Fitting and GAB parameters achieved from ***E*** and ***EHP*** non-linear regression, with confidence intervals of 95%.

Parameters	E			EHP		
	GAB (25ºC)	GAB (30ºC)	GAB (35ºC)	GAB (25ºC)	GAB (30ºC)	GAB (35ºC)
R^2	0,999	0,992	0,994	0,997	0,991	0,998
RMSE	4.6E-4	1.8E-3	1.4E-3	1.1E-3	1.6E-3	6.7E-4
C	56.1±16.2	39.2±33.0	30.1±17.7	24.8±13.6	21.1±18.2	15.2±7.0
X_m	0.0308±0.001	0.0298±0.006	0.0266±0.005	0.0248±0.003	0.0202±0.004	0.0146±0.002
k	0.7836±0.03	0.71±0.2	0.682±0.2	0.7865±0.1	0.8417±0.2	0.9121±0.1
$S(m^2/g)$	128.7	124.6	111.0	103.8	84.4	61.1
ΔH_c (kJ/mol)		47.5			37.4	
ΔH_k (kJ/mol)		10.6			-11.3	
C_0		2.6E-7			7.0E-6	
k_0		1E-2			75.2	
$\Delta H_{s,t}$(kJ/mol)		36.9			48.7	

Table 3. 12 - Fitting and GAB parameters achieved from ***S*** and ***SHP*** non-linear regression, with confidence intervals of 95%.

Parameters	S			SHP		
	GAB (25ºC)	GAB (30ºC)	GAB (35ºC)	GAB (25ºC)	GAB (30ºC)	GAB (35ºC)
R^2	0.997	0.996	0.997	0.997	0.997	0.997
RMSE	7.6E-4	8.4E-4	6.9E-4	7.2E-4	6.9E-4	6.4E-4
C	59.76±60.0	26.36±19.8	12.12±6.5	42.36±40.6	20.21±12.8	8.126±4.3
X_m	0.01507±0.002	0.0136±0.002	0.01247±0.002	0.01241±0.001	0.01175±0.002	0.01179±0.002
k	0.9204±0.07	0.9529±0.08	0.9939±0.08	0.9862±0.06	0.9886±0.07	0.9944±0.08
$S(m^2/g)$	63.02	56.88	52.15	51.90	49.14	49.31
ΔH_c (kJ/mol)		121.88			126.04	
ΔH_k (kJ/mol)		-5.87			-0.63	
C_0		$2.64x10^{-20}$			$3.62x10^{-21}$	
k_0		9.79			1.27	
$\Delta H_{s,t}$(kJ/mol)		127.75			126.68	

Similarly to before, GAB parameters were estimated. The estimate of the monolayer, X_m, as expected, decreased with increasing temperature. When comparing non-treated samples (***E*** and ***S***) with UHP treated samples (***EHP*** and ***SHP***) a decrease of X_m was found. These results are in agreement with the previously discussed decrease in the moisture uptake from virgin fibres treat with and without UHP. Due to the proportionality existing between X_m and S (specific surface area estimate), this last also exhibited the same trend revealed by X_m, i.e. it decreased, with increasing temperature, from non-treated (***E*** and ***S***) to samples treated with UHP (***EHP*** and ***SHP***). Parameter C (from ***E*** and ***S*** to ***EHP*** and ***SHP***, respectively), similarly to before, decreased with increasing temperature, as expected. Also, when comparing non-treated (***E*** and ***S***) with fibres treated with UHP (***EHP*** and ***SHP***), the values where smaller for this last, which, as previously discussed, is related to the lower amount of water molecules required to form the monolayer, due the presence of strongly bound water.

As regards parameter k results, with increasing temperature, the tendency found in ***E*** and ***EHP***, was similar to that encountered on ***R*** and ***RHP***, i.e. for samples not treated with UHP k decreased with temperature, while the opposite was verified on samples treated with UHP. This suggests that in ***E*** the formation of multilayer has a higher contribution to water sorption than in ***EHP*****,** with increasing temperature. Also, when comparing untreated (***E***) with samples treated with UHP (***EHP***), k values were higher in this last. As previously discussed, it is suggested that the presence of strongly bound water may contribute to less intensive water interactions and thus a higher entropy between multilayer water molecules (as k tends to 1, water molecules properties approach those of bulk water).

In the case of softwood virgin fibres, ***S*** and ***SHP***, *k* values revealed a similar trend (increase), on both samples, with increasing temperature. With increasing temperature, in both cases, the multilayer contribution to water sorption becomes less important. This difference, relatively to hardwood fibres, could be attributed to the differences in the type of the fibres studied (different fibres morphology). Nevertheless, upon UHP treatment, from ***S*** to ***SHP***, *k* values increased (nearer 1), which suggests, as discussed for ***E*** and ***EHP***, that the presence of strongly bound water in fibres contributes for the less intensive interactions between multilayer molecules and for its higher entropy.

Similarly to before, from the temperature dependence of *C* and *k*, the parameters, C_0, k_0 and ΔH_c and ΔH_k were determined. Constant C_0 revealed very small values as expected. Parameter k_0 revealed an increase upon UHP, from ***E*** to ***EHP***. This trend is similar to that observed from ***R*** to ***RHP***, indicative of a higher entropy in multilayer water molecules, which endorses the already discussed hypothesis. In contrast with hardwood virgin fibres results, in softwood virgin fibres, from ***S*** to ***SHP***, k_0 decreased, although its value remained higher than 1. This result is indicative of a decrease in the entropy of multilayer molecules on ***SHP***. It is proposed, once more, that this difference in results between both virgin fibres could be related with the differences in morphology existing between both types of fibres.

Parameters ΔH_c and ΔH_k were also estimated from GAB parameters. From ***E*** to ***EHP*** ΔH_c, displayed a decrease from 47.5 to 37.4 kJ/mol. This decrease is in agreement with previous discussed results, since fewer water molecules form the monolayer, lower is the solvation enthalpy registered. In opposite, from ***S*** to ***SHP*** (softwood virgin fibres) a small increase from 121.88 to 126.04 kJ/mol was observed. While in the case of hardwood virgin fibres the results are in agreement with the retraction of the monolayer, in this case, this variation could be attributed to method deviations.[45]

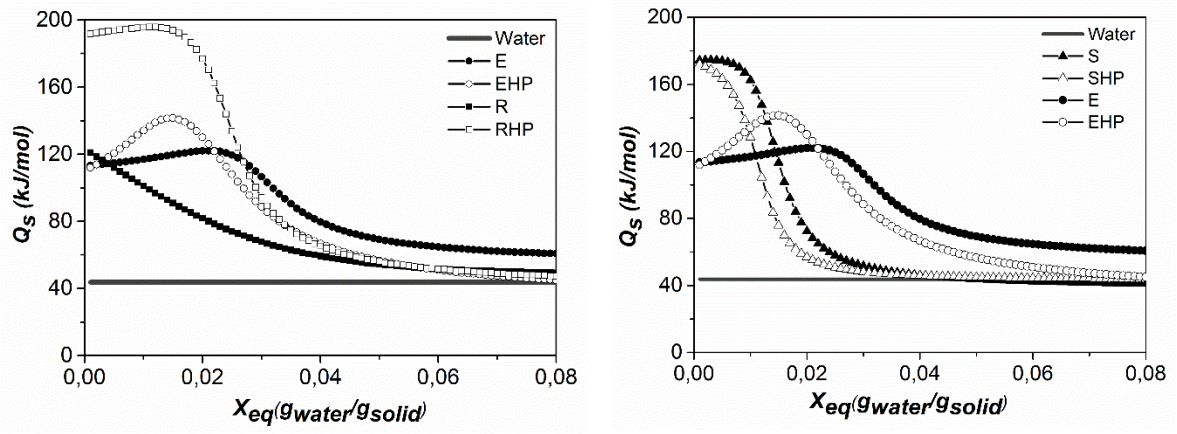
As concerns ΔH_k, divergent results between hardwood and softwood pulps were once more registered. From ***E*** to ***EHP*** a decrease was found, while from ***S*** to ***SHP*** an increase was registered. While in the first case ΔH_k decrease is in agreement with a lower contribution of multilayer to water sorption discussed above, the second suggests the opposite. It is suggested that this divergence in results could be related with methods deviations. It has been reported in the literature[45] that although GAB method is the most recommended to describe cellulosic materials, its parameters may suffer great deviations and still present the same curve, which may explain some of the divergences found.

Nevertheless, considering both ΔH_c and ΔH_k, the net isosteric heat of sorption ($\Delta H_{s,t}$) was also estimated. The results achieved revealed an increase from ***E*** to ***EHP*** (from 36.9 to

48.7 kJ/mol) and a very small decrease from ***S*** to ***SHP*** (ca. 0.8%). Although water uptake was lower from ***E*** to ***EHP***, $\Delta H_{s,t}$ increase could be related to the formation of more intensive interactions with the captured water molecules. In the case of ***S*** and ***SHP*** the decrease observed could be explained by the decrease in the water uptake. Nevertheless, as mentioned above, due to some deviations of the model parameters, these results should be complemented with further studies with other techniques.

It is, however, noteworthy some of the similarities found between the results of recycled fibres and hardwood virgin fibres. As confirmed in fibres characterization, recycled fibres are made mostly of hardwood fibres, therefore this feature may explain the similitude in behaviour between each other results.

The total heat of sorption, Q_s, was also estimated following *Clausius-Clayperon* relationship (Equations 2.5 and 2.6 from ***Chapter 2***, section **2.1.6.1**.) along with GAB fittings for the three types of pulp, with and without UHP.



(a) (b)

Figure 3. 13 – Total heat of sorption determined from *Clausius-Clayperon* relationship and GAB parameters, as function of moisture sorption (a) comparison between ***E*** and ***EHP*** with ***R*** and ***RHP***; (b) comparison between ***S*** and ***SHP*** with ***E*** and ***EHP***).

The total heat of sorption as a function of moisture sorption on the equilibrium (X_{eq}) is represented in Figure 3. 13a for hardwood fibres and recycled fibres and in Figure 3. 13b for both virgin fibres. Recycled fibres exhibited a significant increase in its total heat of sorption, upon UHP, which is in agreement with its improved hydration abilities, as discussed before, although the values cannot be compared.

Virgin fibres results were different between both types of pulps. Hardwood fibres, upon UHP (***EHP***), displayed a maximum that shifted at smaller X_{eq}, with higher Q_s, that afterwards drops until the heat of sorption equals the heat of evaporation of water. Usually, high values of Q_s maximum at low moisture content are associated with strong attraction

forces between active sorption sites and sorbate molecules in the monolayer, whereas lower values of Q_s are associated with weaker interactions.[49] Therefore, it is suggested that the increase in the total heat of sorption at low X_{eq}, in ***EHP***, may be attributed to more intensive interactions, possibly due to the presence of the strongly bound water.

In the case of softwood virgin fibres (***S*** and ***SHP***) total heat of sorption, Q_s, exhibited curves with a maximum near each another. Although ***S*** exhibited a slightly higher one (174.4 kj/mol versus 172.0 kJ/mol), when comparing with ***SHP***. Besides this difference, the sample treated with UHP displayed a narrower curve.

As previously mentioned, it is possible that the observed variances/fluctuations on results could be explained by the variation of the GAB parameters estimated. An example of that includes the fact that constant C varies greatly in magnitude, <10 to >150000, for adsorption and desorption, with little influence on the shape of the isotherm. [45] This variance, as regards the determination of other parameters dependent of C, may affect directly and induce variation on its estimation. Even though GAB model is considered the best choice for fitting pulp and paper moisture sorption isotherms (with constants that have a theoretical meaning), their interpretation sometimes could be less clear, similarly to empirical equations. [45] A way to improve the acquired data would possibly pass through testing more temperatures to ensure a higher accuracy.

3.3.3.4. Calorimetric analysis

Calorimetric analysis was performed to determine the integral heat of wetting, on samples treated with and without UHP. The results achieved are represented in Table 3. 13.

Recycled fibres results, from ***R*** to ***RHP*** revealed an increase in the integral heat of wetting from ***R*** to ***RHP***. These results suggest the presence of more free OH groups for interaction with water, which is in agreement with previous results tendencies, such as the case of moisture sorption isotherms, which brings further confirmation on the ability of UHP regenerating hornified recycled fibres hydration abilities.

As regards virgin fibres, both hardwood and softwood virgin fibres registered a decrease in the integral heat of wetting in samples treated with UHP. The results suggest that less free OH groups were available for interaction with water, as discussed previously, due to the strongly bound water presence. These results endorse previous ones, such as the tendencies observed in moisture sorption isotherms, and allow to confirm the effects brought by UHP on cellulosic fibres.

Table 3. 13 – Integral heat of wetting of samples treated with ***(RHP, EHP, SHP)*** and without UHP treatment ***(R, E*** and ***S)***.

Sample	Heat of Wetting (J/g)
R	43.4
RHP	50.9
E	53.5
EHP	42.8
S	39.4
SHP	33.0

3.3.3.5. Thermal analysis DSC/TGA

Complementary thermal analysis studies were carried out in order to evaluate the changes in the vaporization enthalpy of hydrated samples (conditions of 100 HR%, at room temperature). First, the samples moisture content was determined by TGA, then this data helped to evaluate the vaporization enthalpy by DSC, through the integration of the endothermic peaks corresponding to moisture vaporization (Table 3. 14).

Table 3. 14 – Moisture content and vaporization enthalpy of samples ***R***, ***RHP***, ***E***, ***EHP***, ***S*** and ***SHP***, determined through thermal analysis.

Sample	Moisture content (%)	Vaporization enthalpy (kJ/mol water)
R	12.3	-16.6
RHP	13.6	-15.0
E	14.5	-2.5
EHP	11.8	-19.1
S	15.8	-18.3
SHP	14.3	-63.3

In the case of recycled fibres, the results showed, from ***R*** to ***RHP***, that the enthalpy of vaporization (required to evaporate free water) decreased slightly. It is possible that this result is related with recycled fibres limited macroporosity, and thus a lower presence of free water content. Even though UHP treatment promoted recycled fibres accessibility to free OH groups, these last, as observed in moisture isotherms, help to formation the monolayer, where molecules are interacting strongly with the surface (1^{st} layer) and not easily removed by vaporization. However, it is not clear what happens in the case of free water. Therefore, it is possible the small variation found in the vaporization enthalpy between both samples, are of little significance.

As regards virgin fibres, in both cases, samples subjected to UHP treatment showed higher vaporization enthalpies, when comparing with untreated samples. Contrarily to recycled fibres, virgin ones have higher macropososity. Also, it is possible that the combination of this trait with the increased accessibility to free OH (as result of UHP treatment), may contribute to a higher content of free water. This hypothesis may explain the increases in enthalpy found between non-treated and UHP-treated virgin pulp samples.

3.4. Conclusions

The effects of UHP treatment on different cellulosic fibres (recycled and virgin hardwood and softwood fibres) were demonstrated. The studies allowed to conclude that UHP treatment promoted rearrangements on the studied fibres structure, namely fibril disaggregation, the reverse of fibre collapse, and improved fibres accessibility, into sites previously inaccessible.

The structural changes on fibres were primarily confirmed by XRD, ^{13}CNMR and FTIR of deuterated samples. Here the reorganization of crystalline/amorphous regions upon UHP was demonstrated by the increase of crystallinity and the increase of the average crystallite size. Additionally, it was demonstrated that UHP treatment promotes fibres forced hydration and improved accessibility. While the first is more predominant in virgin fibres, the latter plays a bigger role in the case of recycled fibres. In the case of this last, this implies a decrease on the hornification of recycled fibres and improvement of its properties, such as hydration. These were demonstrated by different tests (such as capillary rise, moisture sorption, the integral heat of wetting, etc). In the case of virgin fibres, the presence of significant amounts of strongly bound water, although it affected the available free OH groups content (as demonstrated by H/D exchange, moisture sorption, calorimetric analysis, etc), it improved hardwood fibres wettability and both types of virgin fibres capillarity.

These results represent an interesting prospect over tissue paper production since they validated the ability of UHP to improve recycled fibres properties, which affects not only the manufacturing process but also the final products features. An example of a manufacture advantage includes the lower zeta potential values of samples treated with UHP, which implies a lower demand of retention aids and even a better retention of other additives such as dyes.

Moreover, the ability of UHP to further improve fibres properties, without mechanical or chemical processing, represents a potential alternative to improve fibres features, such as recycled fibres hydration skills. It is noteworthy that the hydration abilities of fibres are of utter importance for tissue paper.

3.5. References

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Chapter IV

The effect of ultra-high pressure on the papermaking properties of pulp

Contents

4.1. Introduction

The constant demand for improved performance of tissue papers has stimulated companies to develop more effective processes of stock preparation and paper sheet formation, for an improved productivity and quality parameters. Mechanical and physical properties are rather relevant features on this matter, since they outline the end product's performance. To improve these features, changes aimed to improve fibres performance may be considered. [1,2]

The bonding between fibres governs paper sheet properties. This is due to the formation of hydrogen bonds between fibres that are drawn together and oriented by water stream during papermaking. The adequate alignment of fibrils and their bonding between one another, in a paper sheet, provides fibres considerable resistance to being pulled out. This resistance is higher with increasing fibre length, fibre organization and mutual compression on the crossover areas of the fibres, as well as by the cohesiveness of all the fibrils, that are on contacting surfaces and that range in size from the visible to molecular. [2,3] Hemicelluloses on fibres also play an important role on fibre bonding, not only by being present on their surfaces providing sites for interfibre interaction, but also by attracting water into the interior of fibres, softening its structure and turning it less rigid.[2–4]

During papermaking processing many changes occur, yielding losses on pulps properties. These effects affect strongly recycled fibres due to the repetitive cycles of drying, swelling and pressing those were subjected.[5–7] However, drying is still accounted as the main responsible affecting fibres properties. It influences negatively fibre's strength, fibre's swelling and it's bonding, which affects directly paper strength features.[5,8–10] These changes are mainly caused by the hornification effect. As mentioned in previous chapters, hornification occurs due to structural changes on fibres, induced by stressful conditions (such as drying, pressing, etc), which prompts rearrangements on the fibres chains, fibril aggregation resulting in the irreversible deterioration of papermaking properties. In particular, hornification lead to losses on fibres hydration abilities and turns them stiffer. [11,12] In order to decrease the effects of hornification different approaches may be followed, such as chemical treatments with alkaline solutions or beating. [5,7,8,12,13]

The variety of pulp feedstocks available for papermaking made a demand for a fundamental process able to improve fibres quality that can be applied on all types of pulps. With this purpose, pulp beating, one of the main processes used in stock preparation, is often employed.[14]

Pulp beating or refining consists in pulps mechanical modification to achieve pulp properties suitable for papermaking. [14,15]. Its main purposes include improving fibres bonding ability (to form strong and smooth paper sheet), swelling in water, sometimes shorten long fibres for a better sheet formation, or to develop other pulp properties such as absorbency, porosity, or optical properties.[16]

Beating enables fibres to "felt" uniformly, to soften, and to fibrillate, in order to impart strength to paper. The main effects caused by beating include *i)* fines creation; *ii)* internal and external fibrillation; *iii)* fibre cutting or shortening and *iv)* fibres deformation.[3,15,16]Together these effects are able to induce important changes to pulp. Beating improves paper strength properties, prompts a reluctance of fibres to part with water (on the paper machine) and improves the affinity and retention of additives, such as dyes and filling materials. Internal fibrillation, also allows the sorption of additional water around the newly exposed inner surfaces, therefore improving the ability of fibres to interact with water. However, because fibres surfaces are fibrillated, swelling enables fibrils not only to form extra links with adjacent surfaces, (especially if the surfaces are rough), but also to increase fibres bounding area by forming reinforcements around it. [3,14–17]

Ultra-high hydrostatic pressure (UHP) emerges here also as a potential non-degradative treatment able to improve pulp and paper properties. Studies employing UHP on cellulosic fibres have demonstrated the UHP effects on fibres, namely its ability to induce rearrangements on fibrils, yielding fibril disaggregation, and thus higher accessibility into sites previously inaccessible (rearrangements and decrease on fibres hornification). [18–20] Therefore, the effect of UHP pre-treatment of recycled and virgin fibres on the papermaking properties of corresponding pulps was studied. The UHP effect on the pulps beating behaviour was evaluated when the treatment was applied just before the beating or in the middle of the refining process. Simultaneously, the development of strength properties of pulps was assessed.

4.2. Materials and Methods

Cellulosic pulps were provided by Renova, namely Recycled fibres, ***R***, bleached *Eucalyptus Globulus* industrial *kraft* pulp, ***E*** and bleached softwood pulp, ***S***. The pulps used in these studies were the same as mentioned in previous chapter.

4.2.1. Sequences of beating and UHP treatment

The combination of beating with UHP treatment and its benefits was studied according to three different sequences (Table 4. 1): B-HP (beating followed by UHP treatment), HP-B (UHP treatment followed by beating), and B1-HP-B2 (beating at fixed number of PFI revolutions, followed by UHP treatment and finalizing beating).

The three sequences were employed considering fixed UHP conditions (400 MPa, 10 min), and in case of B1-HP-B2, a fixed pre-beating treatment (fixed PFI revolutions) was applied to pulp samples, followed by UHP treatment and by a last beating stage.

Table 4. 1- Sequences of beating and UHP processing carried out using three pulp samples (***E***, ***S*** and ***R***).

Sequences	Fixed Pressure (400 MPa, 10 min)		
	R *(PFI revolutions/no.)*	*E* *(PFI revolutions/no.)*	*S* *(PFI revolutions/no.)*
B-HP HP-B	0-2500	0-6000	0-10000
	Total PFI revolutions (T) =B1+B2		
B1-HP-B2	B1=500 T : 0 – 2500	B1=1000 T : 0 – 6000	B1=1000 T:0-10000

Pressure variation studies were also performed, considering UHP pressure condition of 400 MPa, 500 MPa and 600 MPa, 10 min, at fixed beating conditions (1000 PFI revolutions for ***R***, 3000 PFI revolutions for ***E*** and 6000 revolutions for ***S***)

4.2.2. Hydrostatic ultra-high pressure (UHP) treatment

UHP treatment was carried out with a pulp suspension, dispersed in distilled water (2% consistency), sealed in HDPE flasks, and submitted to hydrostatic high pressure (400 MPa, 500 MPa or 600 MPa), at room temperature (20 ºC), on a Hyperbaric model 55 equipment. Afterwards, if UHP was the last stage of the ongoing sequence, a part of the sample was filtered, air dried (to ca. 8%) and stored, while the other part was directly used to prepare standard handsheets.

In case of samples that were to be subjected to beating, after UHP, these were filtered until they met the conditions required for that step.

4.2.3. Pulp beating

Previous to pulp beating samples weighting 30 g (moisture free) were prepared and then dispersed in agreement with ISO 5263-1:2004. Beating was carried out on a PFI mill according to ISO 5264-2:2011.

4.2.4. Handsheet preparation

When required standard paper handsheets were prepared according to ISO 5269-2, on a Rapid-Köthen (Karl Schröder KG) sheet former.

4.2.5. Physical and mechanical properties analysis

Fibres drainability was tested by analysing the *Schopper-Riegler* degree according to ISO 5267-1:1999. Also the handsheets thickness, density, specific volume and bulk were evaluated according to ISO 534:2011. Tensile index, stretch%, Tear index, burst index, air resistance (Gurley method) and capillary rise, were evaluated in every sample according to, ISO 1924-2:2008, ISO 1974:2012, ISO 2758:2014, ISO 5636-5:2013 and ISO 8787:1986, respectively. Opacity was also evaluated in agreement with ISO 2471:2008.

4.2.6. Fibre analysis

Alterations on fibres morphology were monitored with a Fibre Tester from Lorentzen & Wettre. To do so, 0.2 g of moisture free pulp was dispersed in 200 mL of distilled water. After dispersion was achieved, all suspensions were positioned to be analysed by the equipment, using available software.

4.3. Results and Discussion

4.3.1. Pulp drainability

Hardwood virgin pulp (***E***), softwood virgin pulp (***S***) and recycled pulp (***R***) were submitted to different sequences of beating and UHP treatment, to investigate the benefits brought by the combination of these treatments to fibres properties. The applied sequences were HP-B (UHP followed by beating), B-HP (beating followed by UHP) and B1-HP-B2 (beating pre-treatment at fixed PFI revolutions, followed by UHP and beating) (Table 4. 1). For these tests the pressure applied on pulp suspensions was fixed at 400 MPa (10 min). Pulps drainability was investigated for the three pulp types, as function of PFI revolution (Figure 4. 1).

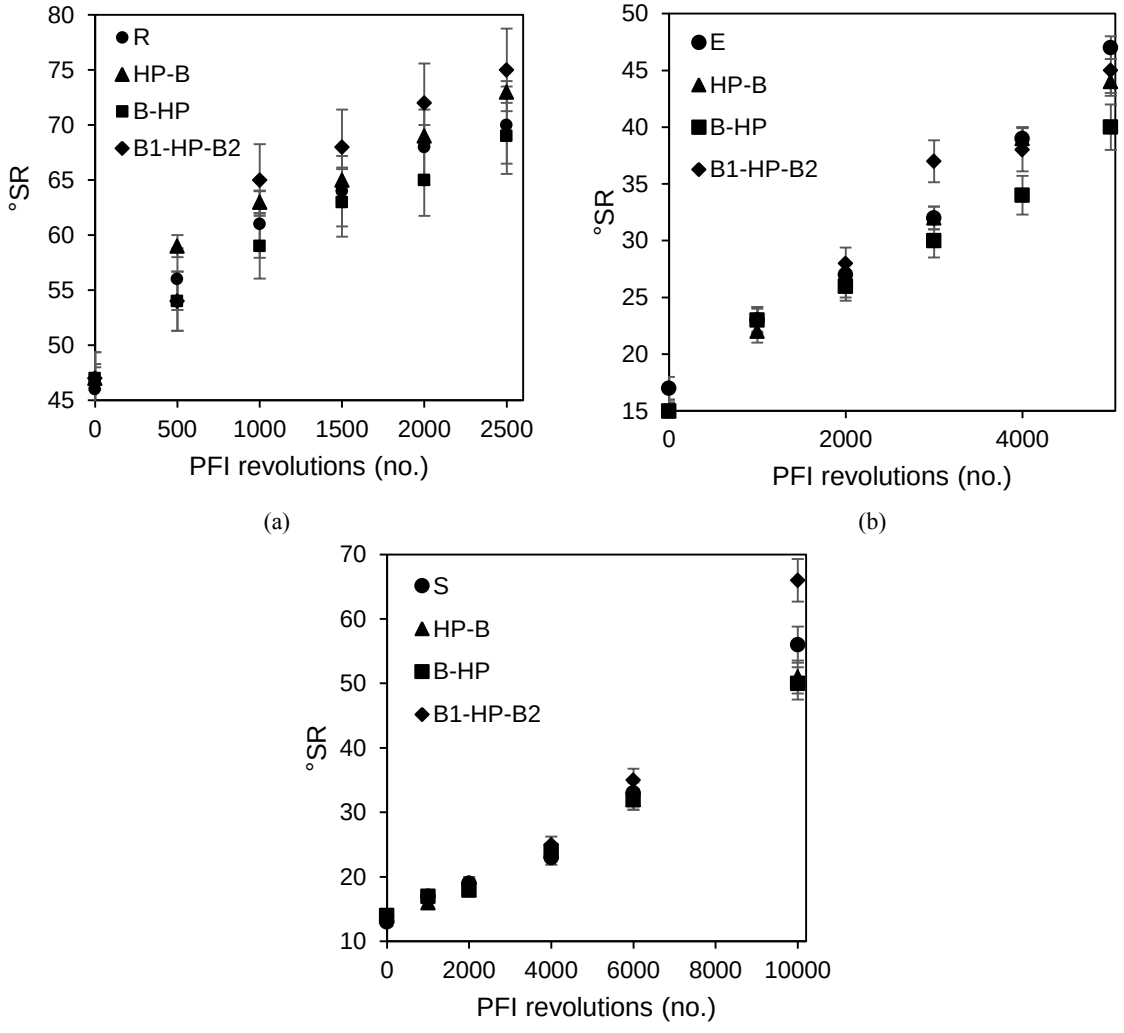


Figure 4. 1 – Drainability as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulp, treated by sequences HP-B, B-HP and B1-HP-B2.

Considering the profiles achieved for ***R*** samples series (Figure 4. 1a), it was found that sequences HP-B and B1-HP-B2 exhibited higher ºSR, with increasing PFI

revolutions, when compared to ***R*** without UHP treatment. The registered increase of ºSR in these trials was up to twice to that without UHP treatment, meaning that half energy may be required to develop fibres into that point. These results in terms of energy cost constitute a rather attractive point, since beating contributes to the major energy consumption in papermaking.

On the other hand, as concerns sequence B-HP, a slight lower values of ºSR were registered, with respect to ***R***, which was attributed to UHP treatment as the last stage. It has been demonstrated in previous chapters and literature[20] that UHP induces fibril disaggregation and forced hydration, causing fibrils enlargement. This explains the results achieved by B-HP, since fibres are "bulkier", there is more vacant space between one another, being easier for water to drain.

At the same time, by applying beating after UHP treatment (HP-B) it seems that fibres became more susceptible to beating (enhanced fibre accessibility caused by UHP treatment) and thus, higher fibrillation may be achieved. These events are in agreement with the increased water draining resistance (higher ºSR values). Similarly, the same justification may be used to explain the behaviour in B1-HP-B2 sequence. In this case, the initial beating stage fibrillates fibres, which after UHP become "bulkier", being more accessible to water (UHP effect). At the last beating stage, further fibrillation took place, which explains the substantial increase on beatability, and therefore the increased resistance to water draining.

In case of virgin fibres ***E*** and ***S*** (Figures 4. 1b and c, respectively), sequence B1-HP-B2, registered a slight increase on ºSR between 2000 and 4000 PFI revolutions and as high as 6000 PFI revolutions, respectively. The other two sequences (B-HP and HP-B), in both cases (***E*** and ***S***) displayed either slightly lower or similar ºSR values. The use of UHP treatment after beating, and thus fibres enlargement (due to forced hydration), explain the decrease of ºSR. Since fibres became "bulkier", with less hydration capacity more non-bond water is available, thus favouring the water draining. The beating after UHP treatment (HP-B) results, for hardwood virgin pulps (***E*** pulps), showed slightly lower or similar ºSR relatively to untreated pulp, ***E***. Overall again B1-HP-B2 sequence enabled the higher increase on ºSR values, for the three evaluated pulps.

4.3.2. Fibre Morphology

Variations on fibres morphology were also analysed by parameters such as weight-average length (L_w), coarseness, and mean kink index. These parameters were analysed at fixed beating conditions (1000 PFI revolutions for ***R***, 3000 PFI revolutions for ***E*** and 6000

PFI revolutions for ***S***), and at fixed pressure conditions (400MPa, 10min), for all sequences.

Table 4. 2 display the results obtained for recycled fibres (***R*** samples). As concerns the fibre length, only upon sequence B1-HP-B2 a decrease in fibres length was registered. This may be attributed to fibres shortening induced by the 2nd step of beating, probably due to the increased coarseness of fibres after UHP processing. In fact, an increase of coarseness was registered, of 29% and 28%, from ***R*** to HP-B, and from ***R*** to B-HP, respectively (Table 4. 2). The use of UHP may explain these increases, since, as mentioned before, it provokes forced hydration and thus fibrils enlargement (cell wall enlargement).[20] However, in the sequence B1-HP-B2, the final coarseness was diminished in relation to HP-B and B-HP segments, due to fibre wall dilapidation, result from the synergetic effect of UHP treatment with two beating stages.

Mean kink index results revealed a decrease from ***R*** to HP-B, and from ***R*** to B-HP, of 30% and 28%, respectively. The decrease of the number of deformations in fibres could be associated to the combination of effects brought by UHP treatment, (disaggregation and forced hydration) and beating (fibres straightening).

Table 4. 2 – Fibres analysis parameter, for non-treated ***R***, and ***R*** submitted to sequences HP-B, B-HP and B1-HP-B2 at fixed conditions (400MPa, 10min and 1000 PFI revolutions)

Sample	R	HP-B	B-HP	B1-HP-B2
L_w (mm) ± 0.004	0.86	0.86	0.86	0.82
Coarseness (µg/m) ± 1.0	146.5	189.3	187.6	132.3
Mean kink index ± 0.008	2.65	1.87	1.90	2.53

Virgin pulps ***E*** and ***S***, were also analysed for variations on fibre morphology. The results achieved are represented in Table 4. 3. As concerns fibres length, ***E*** samples did not register significant variations. In opposite to recycled fibres, virgin hardwood fibres are less damaged. Thus, it is possible that hardwood virgin fibres (short fibres) are not as affected by fibres shorting and cutting during beating, as recycled fibres (made majorly form hardwood fibres, as determined in ***Chapter 3***). Also for being short they may be less prone to deformations relatively longer fibres. As regards ***S*** samples, slight variations were verified within the error of determination.

Coarseness results, similarly to length, revealed small variations on ***E*** samples, upon the different sequences of refining. Due to UHP treatment, in B-HP and HP-B sequences a higher coarseness was registered, than with unbeaten pulps, which is in agreement with UHP aptitude for forced hydration and fibril enlargement. However, upon B1-HP-B2, the combination of two beating sequences with UHP reduced coarseness, due to an improved

beating efficacy (higher cell wall dilapidation). Like hardwood virgin fibres, softwood virgin fibres, ***S***, exhibited a similar behaviour. This result may be explained by the hypothesis used to discuss hardwood virgin fibres results.

Mean kink index data exhibited its decrease in hardwood virgin fibres, ***E***, deformations (such as wrinkles or knees) (ca. 15%) for B-HP and an increase (ca. 11%) in case of HP-B. As for B1-HP-B2, this last did not exhibited relevant variations. These results suggest that UHP as last stage, enabled fibre straightening and the decrease on the fibres deformations. Thus it is possible that improved straightening of fibres thanks to UHP forced hydration and fibres enlargement could explain the results achieved.[20]

As regards the mean kink index results for ***S*** fibres, the variation found displayed rather variable behaviour. This variation could be ascribed to their length and thus variable behaviour towards both UHP and beating.

Table 4. 3 - Fibre analysis parameters, for non-treated ***E*** and ***S***, along with ***E*** and ***S*** subjected to sequences HP-B, B-HP and B1-HP-B2, at fixed conditions (400MPa, 10min, with 3000 PFI revolutions for ***E*** and 6000 PFI revolution for ***S***)

	E	HP-B	B-HP	B1-HP-B2
L_w (mm)± 0.005	0.75	0.75	0.76	0.75
Coarseness (µg/m) ± 1.3	84.6	86.5	85.1	83.3
Mean kink index ± 0.02	2.26	2.50	1.92	2.22
	S	HP-B	B-HP	B1-HP-B2
L_w (mm) ± 0.01	1.78	1.79	1.79	1.78
Coarseness (µg/m) ± 1.2	181.3	192.7	193.1	180.3
Mean kink index ± 0.01	1.73	2.29	1.49	2.28

4.3.3. Physico-mechanical properties

Paper physical and mechanical properties were also studied on samples untreated (***R***, ***S*** and ***E***) and treated by sequences HP-B, B-HP and B1-HP-B2.

The bulk of handsheets (cm^3/g) was examined for each beating sequence. As regards ***R*** samples (Figure 4. 2a), a decrease of bulk in HP-B and B1-HP-B2 sequences was observed, comparatively to ***R***, while, in case of B-HP, a slight increase was found. These results suggest that the first two sequences were able to produce denser handsheets, while B-HP revealed the opposite effect.

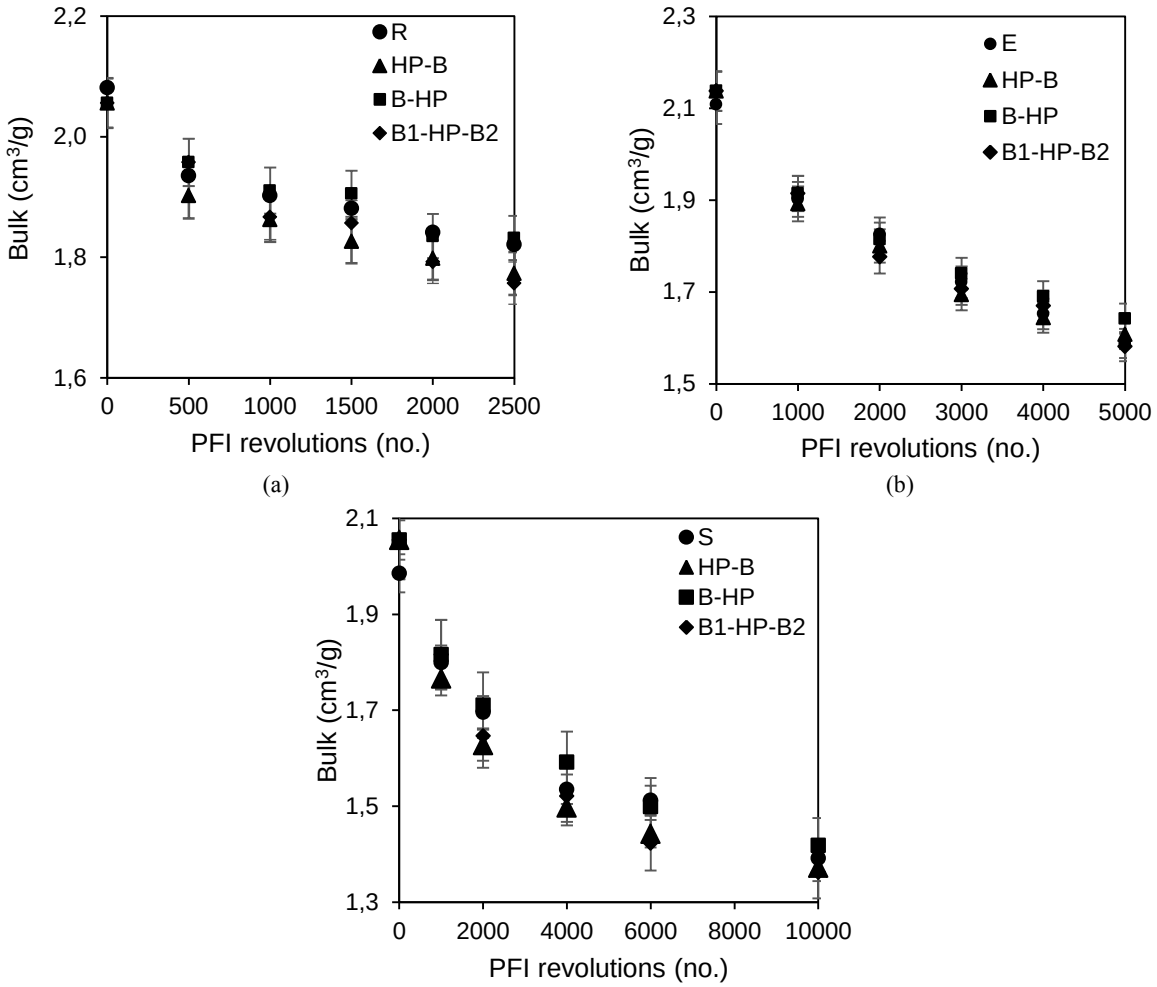


Figure 4. 2 – Bulk (cm^3/g) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulps, treated by sequences HP-B, B-HP and B1-HP-B2.

An explanation for the increased paper density may be related with increased fibres fibrillation (resulting from beating), which agrees with increased ºSR values (Figure 4. 1). Besides, beating favoured fibres plasticity and compressibility for a more efficient packing of fibres, enabling the formation of dense handsheets, as seen after HP-B and B1-HP-B2 sequences.

On the other hand, applying UHP after beating (B-HP) showed different features, suggesting that beating let fibres became more accessible during UHP treatment to forced hydration. As result from this last, fibres become "bulkier" (fibres enlargement) creating higher porosity on handsheet network, and thus decreased density.

Hardwood virgin fibres, ***E*** samples (Figure 4. 2b) revealed no significant bulk variations in different beating sequences. Here results from different treatments were quite similar. This difference, relatively to recycled fibres, could be related to strong hornification of recycled fibres possessing already damaged cell walls.

In the case of softwood fibres (Figure 4. 2c), despite the similarity of conventional beating (***S***) and those with UHP treatment, some lower bulk values were detected after HP-B and B1-HP-B2 beating sequences. This result suggests denser handsheets due to an efficient packing and interfibre interaction of fibres, caused by beating after UHP treatment (fibres fibrillation).

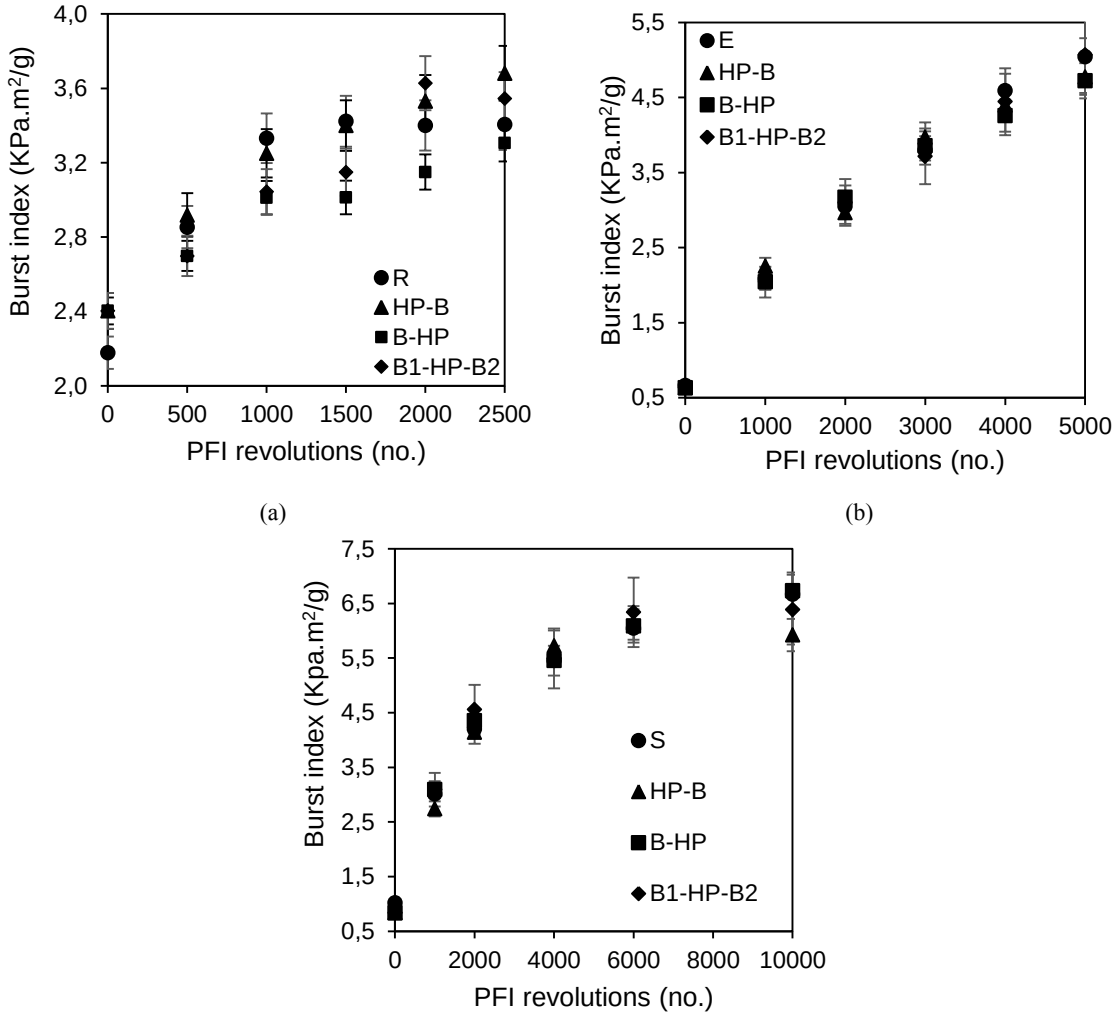


Figure 4. 3 – Burst index (KPa.m^2/g) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulps, treated by sequences HP-B, B-HP and B1-HP-B2.

Burst index was also evaluated as a function of PFI revolutions. Recycled fibres samples, ***R***, (Figure 4. 3a), displayed a slight increase of burst index in sequence HP-B, from 1500 revolutions onwards. Also, a similar behaviour was observed for B1-HP-B2. These increases suggest that UHP treatment when applied between beating stages, improved interfibre bonding. On the contrary, B-HP sequence revealed a decrease of burst index with increasing of PFI revolutions, which could be attributed to an efficient forced hydration of fibres, thus forming bulk network with decreased overlapping area of fibres.

The intrinsic frailty of recycled fibres also may have contributed to the handsheet fibre network of refined pulp.

As concerns both virgin ***E*** (Figure 4. 3b) and softwood ***S*** fibres (Figure 4. 3c), little variations were found along beating in all sequences. These little variations may be attributed to the virgin fibres intact cell wall, before the treatments, contrarily to recycled fibres (beaten and damaged fibres). In other words, the effect of UHP in different beating sequences was levelled out.

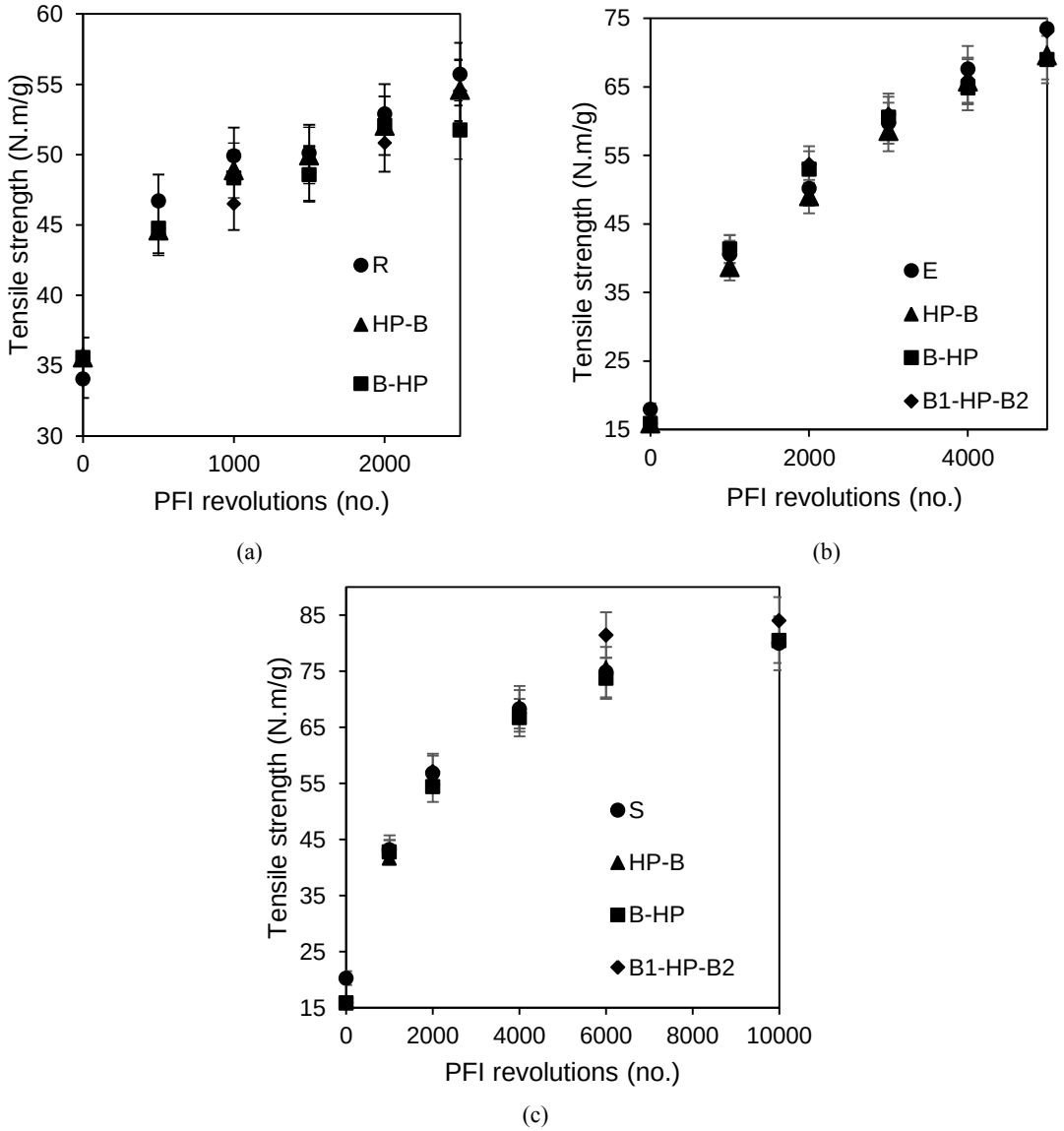


Figure 4. 4 - Tensile strength (N.m/g) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulps, treated by sequences HP-B, B-HP and B1-HP-B2.

Tensile strength for ***R*** samples (Figure 4. 4a) revealed a slight decrease after all beating sequences, relatively to untreated ***R***. This fact contradicts the slightly decreased bulk of handsheets beaten in HP-B and B1-HP-B2 sequences, which may be explained by

intrinsically damaged recycled fibres having weak points in fibres that did not allowed the increase of handsheets strength.

The tensile strength of virgin pulps, ***E*** (Figure 4. 4b) and ***S*** (Figure 4. 4c), did not vary significantly, along with the beating in all applied beating sequences. This is in tune with the beating behaviour of fibres (Figures 4. 1b and c) and the bulk of handsheets (Figures 4. 2b and c) of virgin fibres, refined with and without the application of UHP in beating sequences.

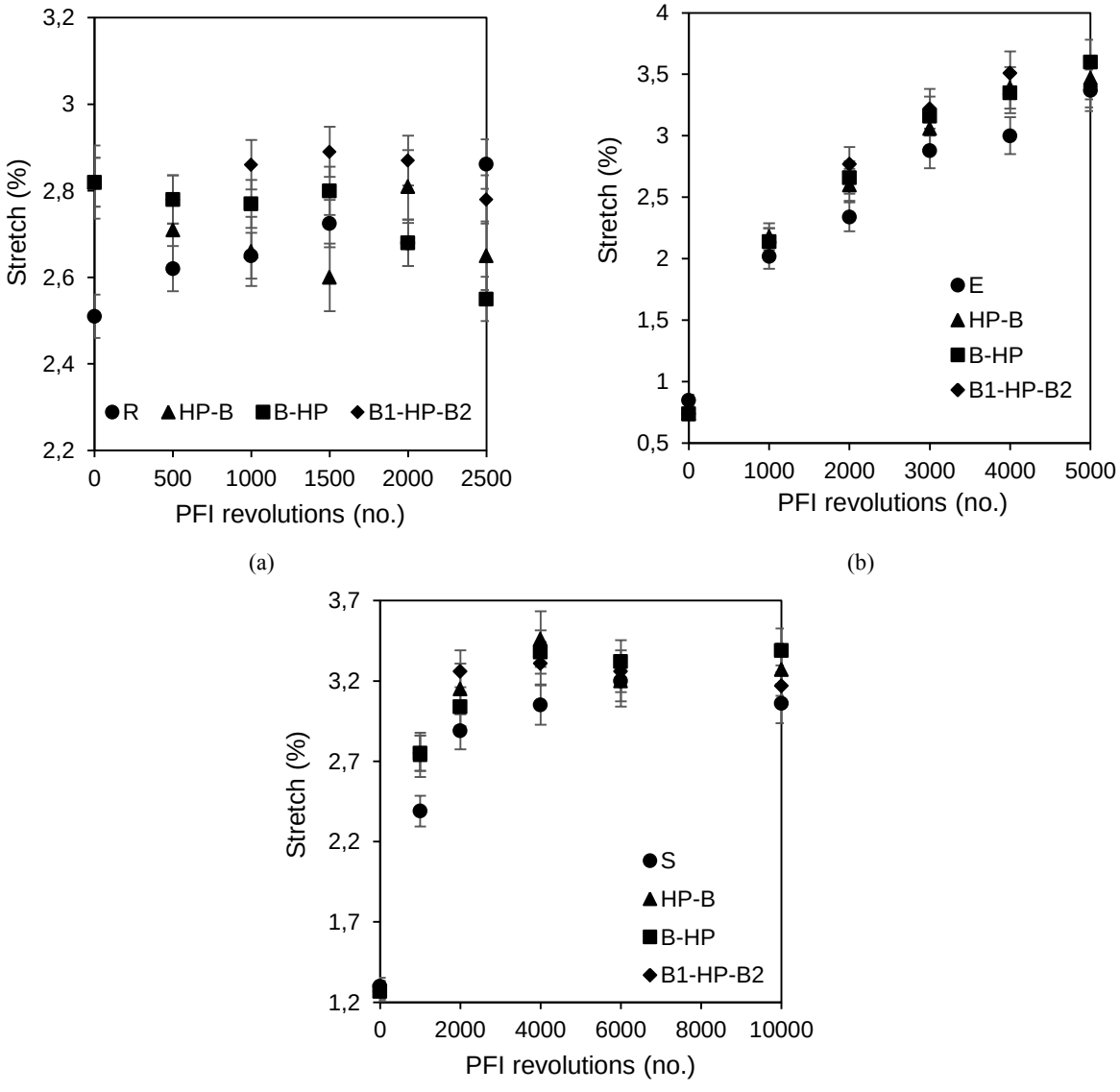


Figure 4. 5 – Stretch (%) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c), treated by sequences HP-B, B-HP and B1-HP-B2.

The analysis of stretch (%) as a function of PFI revolution for ***R*** samples (Figure 4. 5a), revealed an improved elasticity of fibres network in handsheets, when applying the UHP steps in the refining scheme. This is a result of forced hydration of fibrils, thus improving their plasticity.

E samples (Figure 4. 5b) also registered slightly higher stretch % in all three beating sequences, especially in B1-HP-B2. Again, it may be suggested that UHP treatment promoted the plasticity and elasticity of fibres. A similar trend was verified for ***S*** samples (Figure 4. 5c), which was especially notable up to 6000 revolutions. The differences between recycled and virgin fibres may be explained, if recalled, by the fact that the former ones are already beaten and possess a damaged structure, while the latter ones originally exhibit an intact fibre wall. Thus, upon UHP treatment recycled fibres may develop drainability and be modified easier and more extensively than virgin fibres.

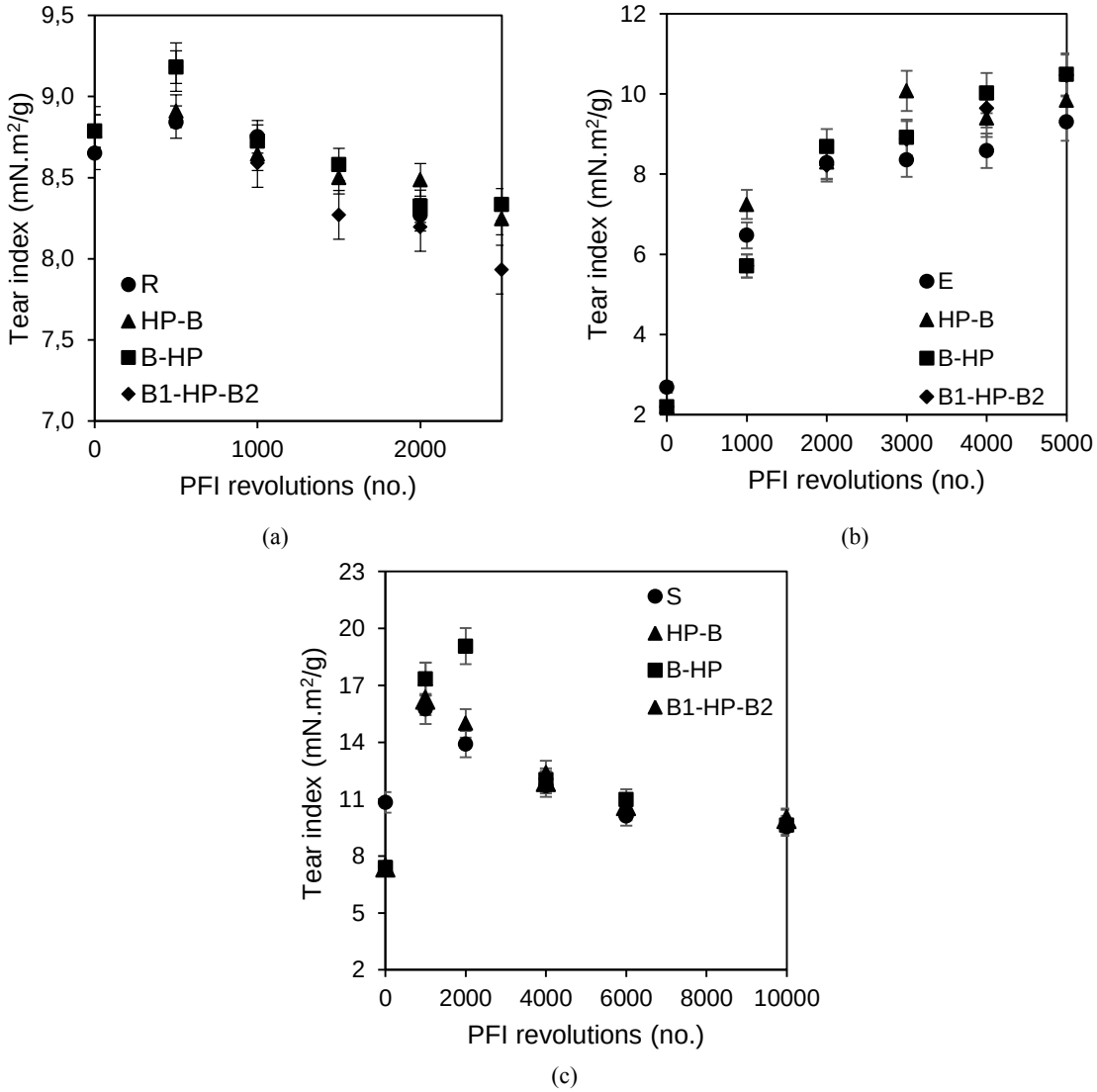


Figure 4. 6 - Tear index (mN.m^2/g) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulps, treated with sequences HP-B, B-HP and B1-HP-B2.

The tear index was also evaluated and the results for ***R*** samples are displayed in Figure 4. 6a. It was found, for all beating sequences, that tear index increased along beating, when UHP was implemented. Although, this increment was not so high (ca. 5%), it may be concluded that UHP treatment improved interfibre bonding in paper network.

Virgin fibres also exhibited an increase of tear index values (Figure 4. 6b), for all beating sequences containing UHP stages. In the case of ***E*** pulp, the sequence displaying the highest increase varied with beating development, while with ***S*** pulp (Figure 4. 6c) samples beaten by B-HP were the ones exhibiting the highest tear index values (ca. 40% increase at 2000 revolutions). These results demonstrated the potential of UHP processing to improve fibres bonding, due to the synergetic effect of UHP with beating (improved accessibility imparted from UHP processing and enhanced fibrillation efficiency in beating).

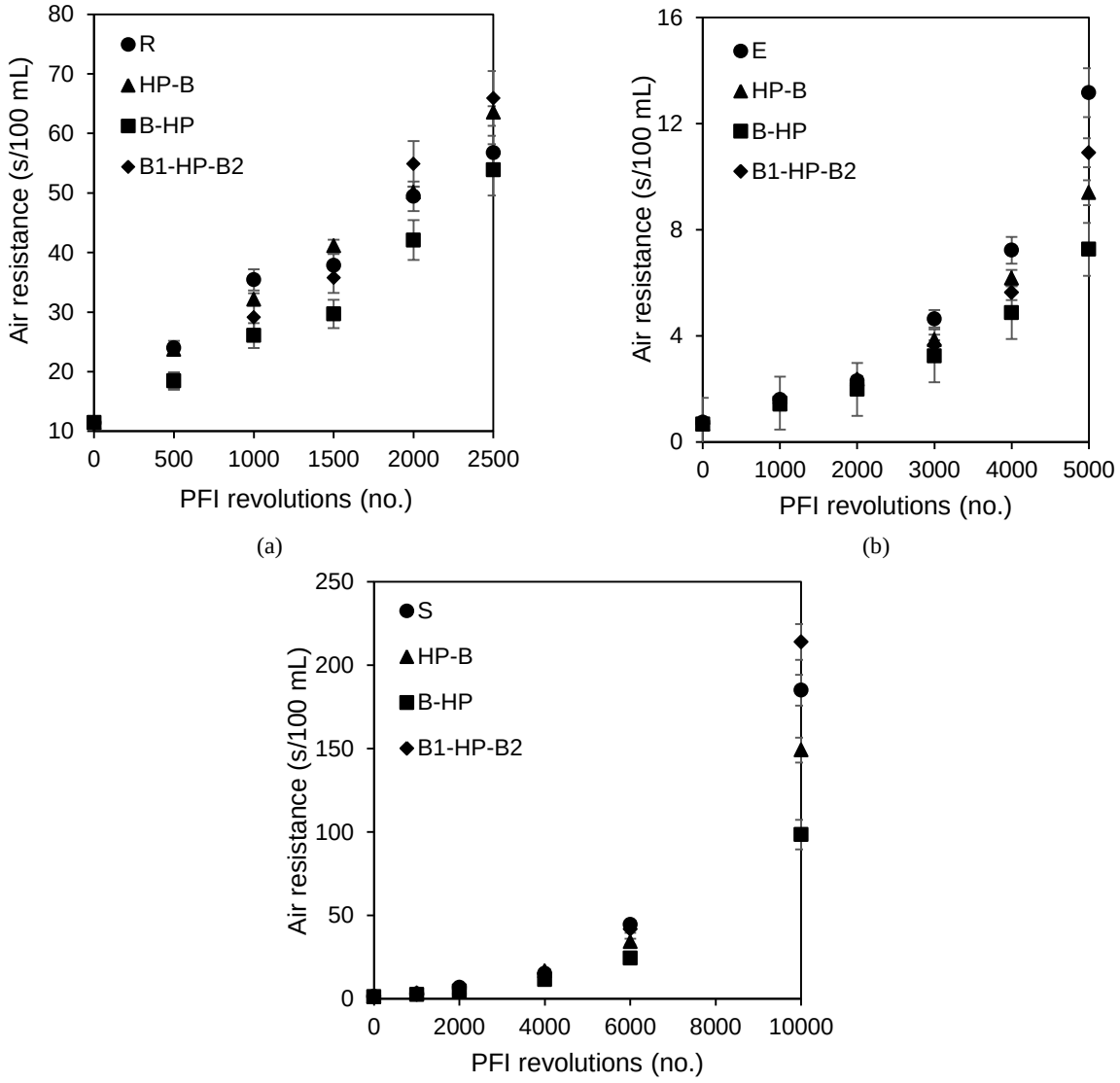


Figure 4. 7 – Air resistance (s/100 mL)) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c), treated by sequences HP-B, B-HP and B1-HP-B2.

Gurley's resistance to air permeation was also determined for both recycled and virgin fibres. The beating results of ***R*** pulp, presented in Figure 4. 7a, displayed slightly lower values until 1500 revolutions. However, the improvement in air resistance was not

so evident for the high beating degrees (>2000 revolutions), especially for HP-B and B1-HP-B2 sequences. These observations, in general, indicated the increase of paper porosity, while applying UHP before, and, especially, after beating. This is in tune with increased bulk of pulp handsheets, upon last UHP stage, in the beating sequence. It is thus understandable that coarser and bulkier elastic fibres form more porous network, than less coarse and plastic fibres possessing increased contact area.

Similar features were found for virgin fibres in ***E*** and ***S*** pulps (Figures 4. 7b and c), especially when high refining energies are involved (>2000 revolutions for ***E*** and >6000 revolutions for ***S***). It is possible that in the case of ***S*** (softwood fibres), by applying UHP conjugated with two beating stages, higher impact on fibres is achieved (more fibrillation, deformation, fibres shortening, cutting, fines formation), rendering higher bonding area improved fibre packing, and thus less vacant sites (less porosity).

It may be also claimed that differences found between the beating sequences for recycled fibres and virgin fibres could be related with the fact that recycled fibres were already beaten in the past.

4.3.4. Optical properties and capillarity

Other properties were also evaluated to complement previous data. These properties include opacity (an optical property) and capillarity (measure of paper hydration abilities). The dependence of optic properties, i.e. opacity and capillarity for different beating schemes with UHP were also evaluated.

As could be expected, pulps refined in conjugation with UHP stages demonstrated high opacities than conventional beaten pulps (Figure 4. 8). The highest increase of opacity was registered when the beating sequence was before UHP treatment (B-HP and B1-HP-B2). This can be explained by bulkier pulps fibres obtained in these sequences (Figure 4. 2). The highest light reflectance was observed for the recycled fibres. The highest effect of UHP stages on the opacity increment was also obtained for recycled pulp (Figure 4. 8). This fact may be justified by the presence of residual fillers not eliminated completely from recycled pulp upon purification.

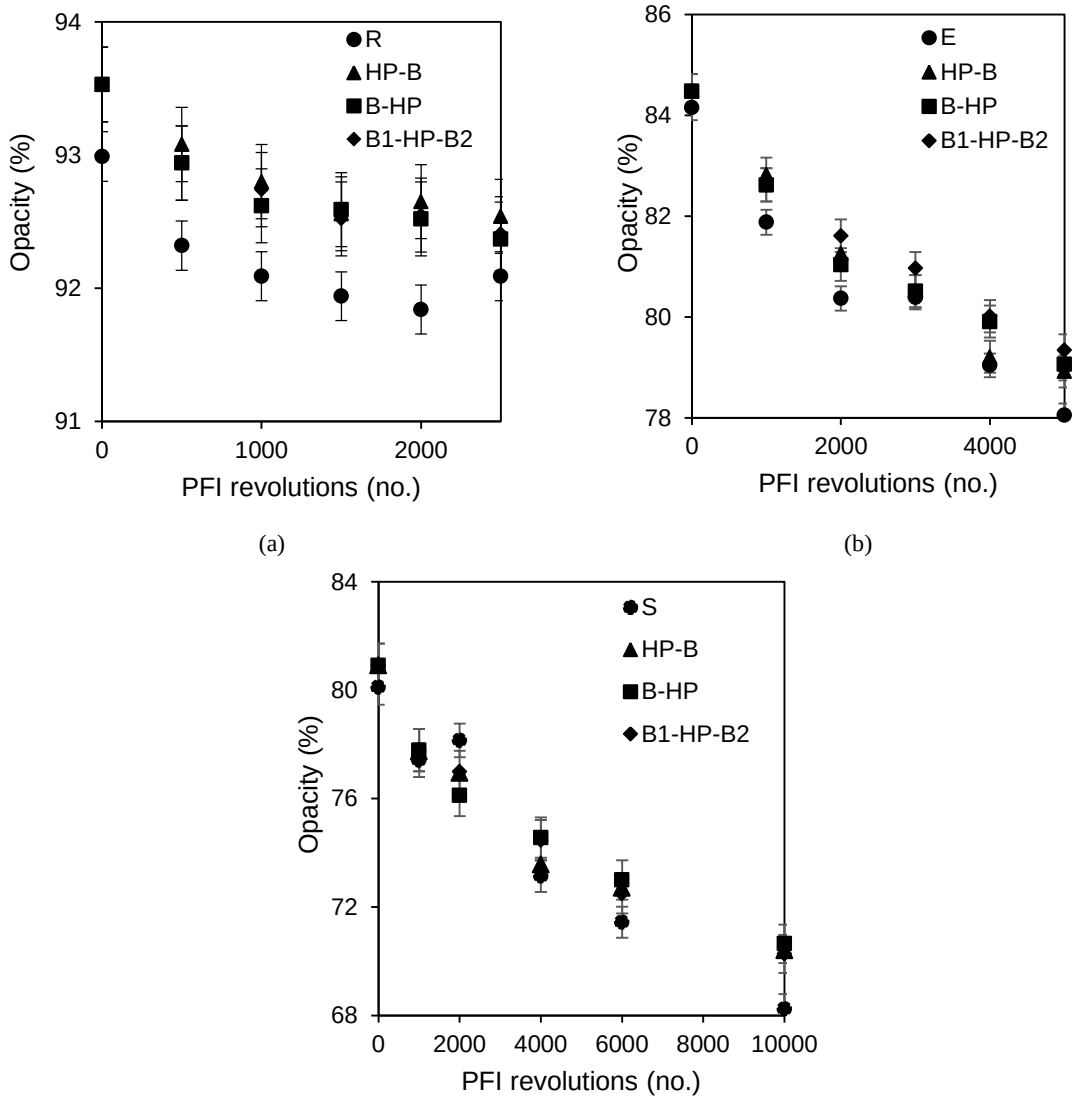


Figure 4. 8 – Opacity (%) as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulps, treated with sequences HP-B, B-HP and B1-HP-B2.

Variations on fibres hydration skills were also studied by capillarity tests. ***R*** pulp (Figure 4. 9a) demonstrated a strong tendency to increase capillarity when combining the beating and UHP steps. The best results were obtained when UHP stage followed the beating stage (B-HP and B1-HP-B2), where capillarity increased almost double (e.g. at 1000 revolutions). These facts were related with increased paper porosity, while subjecting pulp to UHP, especially after beating. As known, the capillary forces depend on the liquid-air surface tension (γ), on the cosine of contact angle between liquid and capillary surface ($\cos\theta$), and are reversibly proportional to the radium of the capillary (r). This relationship is represented in Equation 4.1, where ρ is the density, and g is the acceleration due to gravity.[21,22] Hence, besides eventual changes in capillary diameters, in formed handsheets,

the improved hydrophilicity of fibre surface (***Chapter 3***, Table 3.8) after UHP treatment will improve the sorption of paper material.

$$h = \frac{2\gamma \cos\theta}{\rho g r} \qquad \text{Equation 4. 1}$$

As regards virgin fibres (***E*** and ***S*** samples in Figures 4. 9b and c, respectively), overall, capillarity tests demonstrated that the combination of UHP with beating enabled an improvement of capillary rise. Again, sequences B1-HP-B2 and B-HP produced fibres with higher capillary rise, than after HP-B sequence.

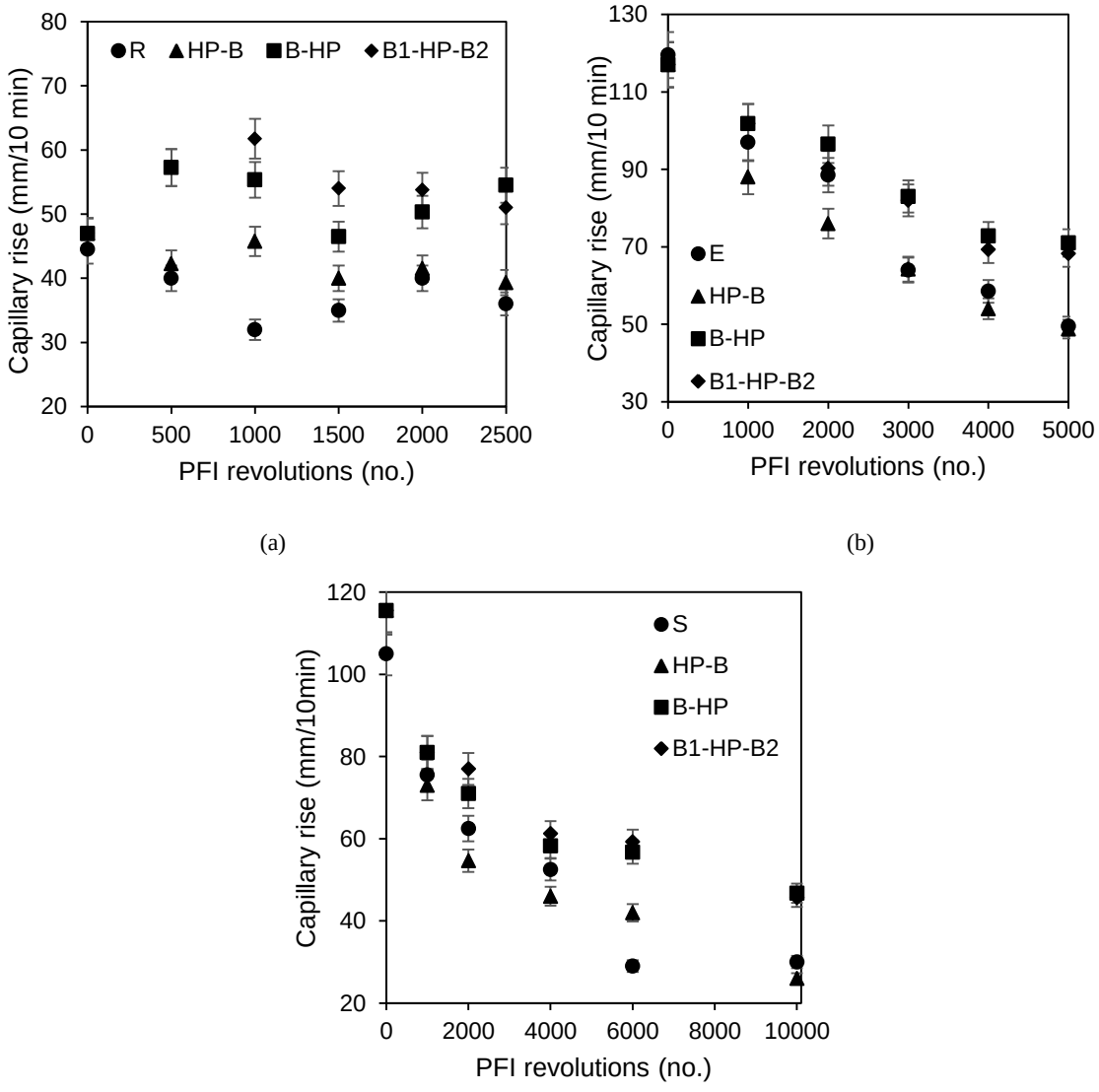


Figure 4. 9 – Capillary rise as a function of PFI revolutions of ***R*** (a), ***E*** (b) and ***S*** (c) pulps, treated by sequences HP-B, B-HP and B1-HP-B2.

The results found for ***E*** and ***S*** samples series (virgin fibres) differed from those of ***R*** samples series. The increase in capillarity was not as expressive as that seen on ***R*** (recycled fibres). Also it is important to remember that these last exhibit higher hornification,

degradation and impurities content. Therefore, the synergetic effect of UHP and beating, promoted the reduction of the negative effects brought by hornification (such as limited water uptake, weaker physical/mechanical properties). The variations found on this parameter for ***R*** samples were, as expected, more substantial, than those found on virgin fibres (***E*** and ***S***).

4.3.5. Effect of UHP conditions on the pulp beating

4.3.5.1. Properties

The physical and mechanical properties were further analysed considering increased pressure conditions (500 and 600 MPa) at fixed beating conditions (for ***R*** at 1000 PFI revolutions, for ***E*** at 3000 PFI revolutions and for ***S*** at 6000 revolutions). Similar to before drainability, bulk, burst index, tensile strength, stretch (%), tear index, air resistance, opacity (%) and capillarity were evaluated.

Results of drainability as function of pressure (ºSR versus pressure), are shown in Figure 4. 10a for ***R*** samples series. The results revealed that, when pressure was risen, HP-B sequence displayed always increased beating degree values. Also, B1-HP-B2 sequence exhibited increased beating degree values with a maximum at 500 MPa, followed by a decrease at 600 MPa. As for B-HP, the decrease already registered at 400 MPa was further boosted. These values could be indicative that employing higher pressures could lead towards stronger UHP effects on sequence treatments.

In the case of ***E*** samples (Figure 4. 10b), overall higher pressures prompted a small and not very significant decrease of beating degree, except for B1-HP-B2, which increased at 400 MPa. For 500 MPa and 600 MPa the beating degree values were near those of untreated sample or slightly lower. As for HP-B the variations were not significant. Similarly, ***S*** pulp fibres (Figure 4. 10c) also exhibited lower or similar results to untreated pulps, with exception of HP-B at 500 MPa and B1-HP-B2 at 400 MPa.

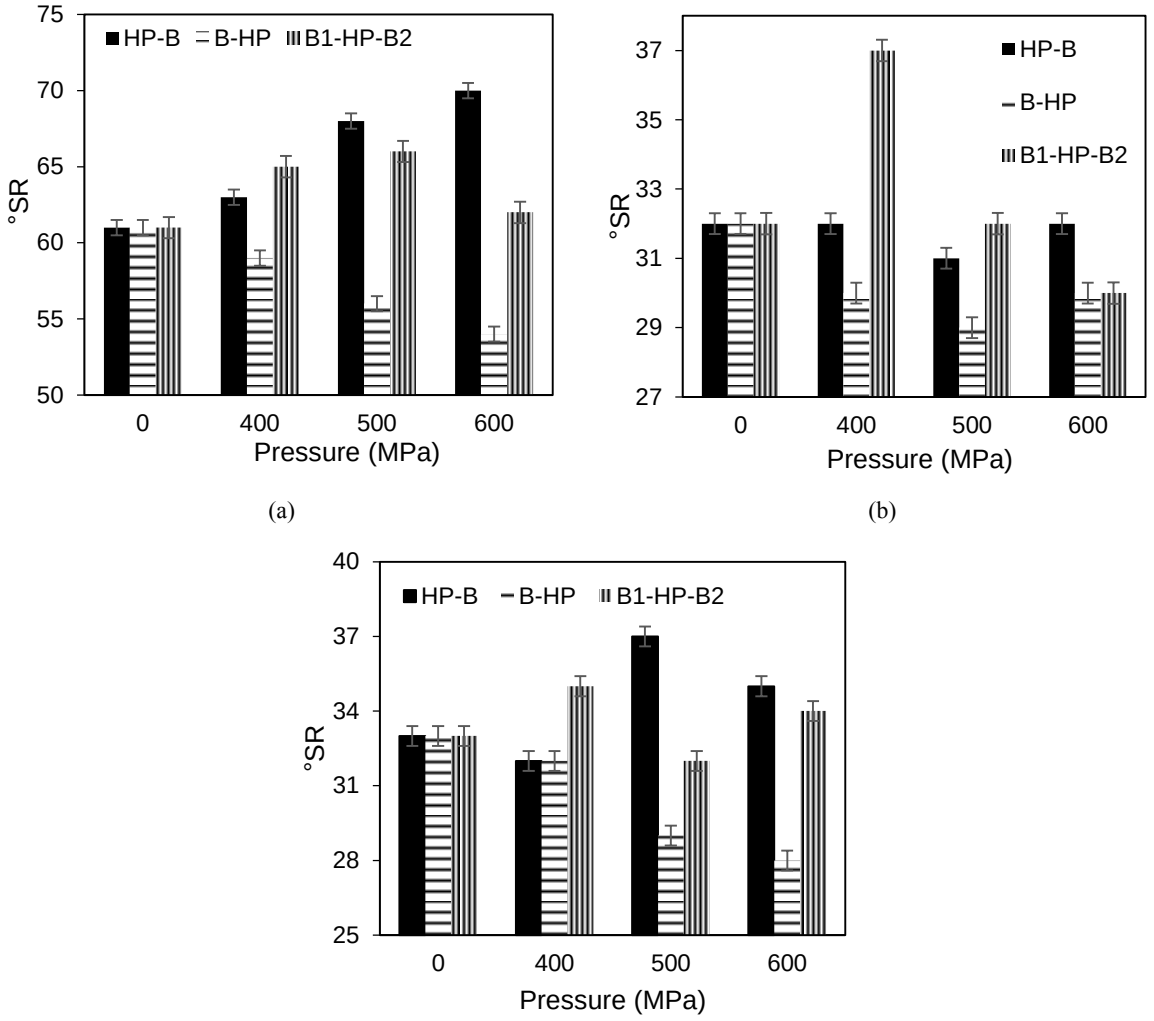


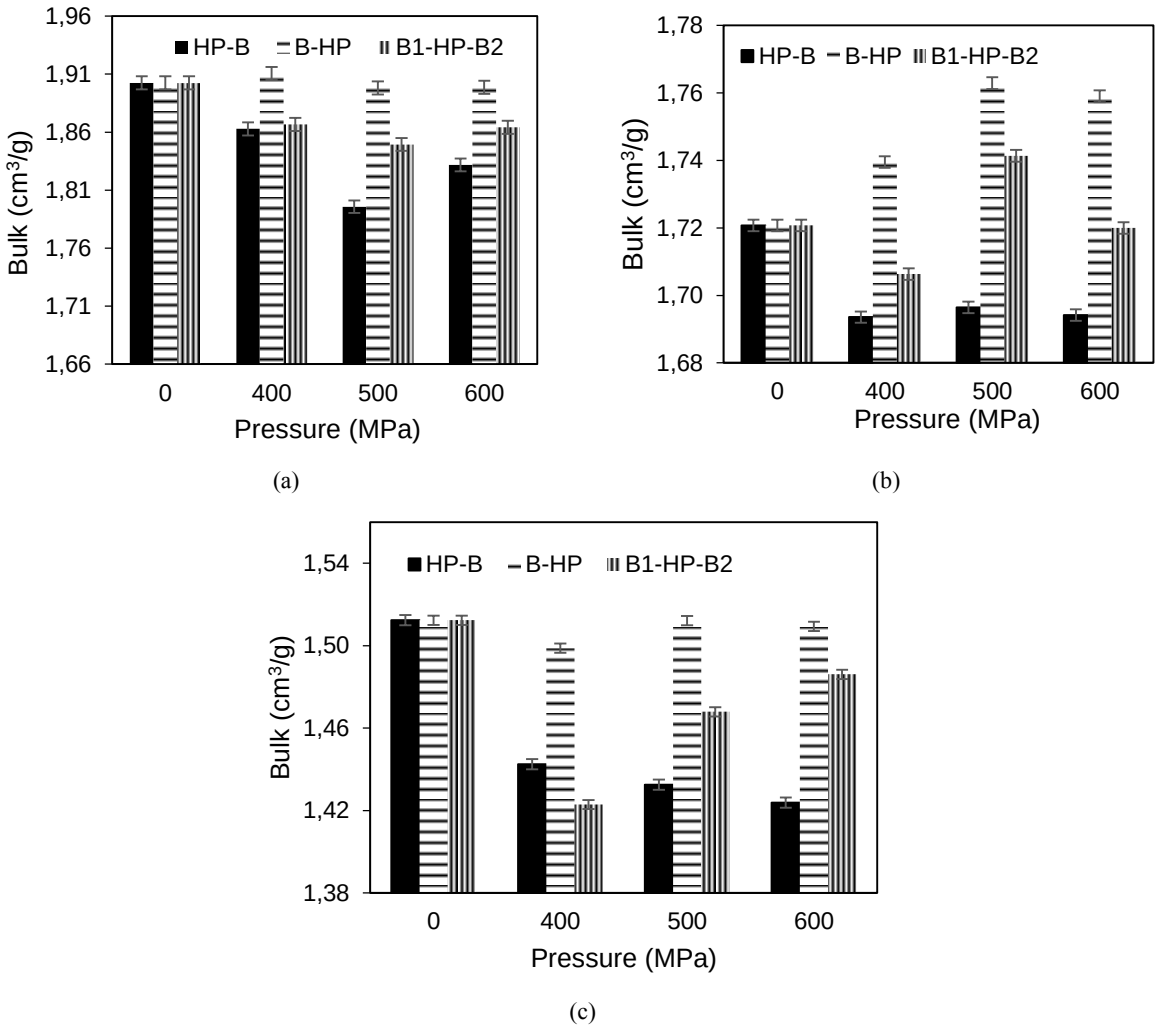
Figure 4. 10 - Drainability of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

Bulk was also analysed for pressure conditions between 400 and 600 MPa. In the case of ***R*** samples series, (Figure 4. 11a), sequences HP-B and B1-HP-B2, from 400MPa to 500 MPa and 600 MPa, exhibited a small decrease of bulk values, with a minimum at 500 MPa. At the same time, B-HP sequence did not exhibit significant variations. Also, B-HP sequence displayed similar results to untreated pulp. In the case of low bulk values, dense handsheets are formed possibly due to an improved fibres plasticity (synergetic effect of UHP and beating, as previously discussed).

As concerns ***E*** samples series (Figure 4. 11b), at increased pressure, an increase in bulk was found in B-HP sequence and to some extent, in B1-HP-B2 sequence, while in the case of sequence HP-B, lower or similar bulk results were registered. It may be claimed, again, that the application of UHP stage after the beating step led to the bulk increase progressively with pressure. The increases found on bulk are related with UHP aptitude for

forced hydration and thus fibres enlargement. The same did not occur upon the other sequences due to beating as the end stage, of multi-beating stages (B1-HP-B2).

Similarly to ***R***, ***S*** samples series (Figure 4. 11c) also displayed a similar behaviour (low bulk values) after UHP treatment, although, in this case, this is not related with the damaged structure of fibres.



(a) (b)

(c)

Figure 4. 11 – Bulk(cm^3/g) of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

The burst index of handsheets produced from refined pulps was also analysed as function of pressure. ***R*** samples series (Figure 4. 12a), at increased pressure conditions (from 400 to 600 MPa), registered either similar or slightly lower variations on burst index. Furthermore, ***E*** samples (Figure 4. 12b), displayed similar or slightly higher tensile index (HP-B and B1-HP-B2 sequences). It seems that the application of UHP stage before beating led to bulkier handsheets with improved interfibre bonding.

In the case of long fibres, ***S*** sample series (Figure 4. 12c), here a notable increase in burst index was found, meaning that the synergetic effect between beating and UHP was

attained, yielding a more efficient fibrillation on softwood fibres during the beating of UHP pre-treated pulp.

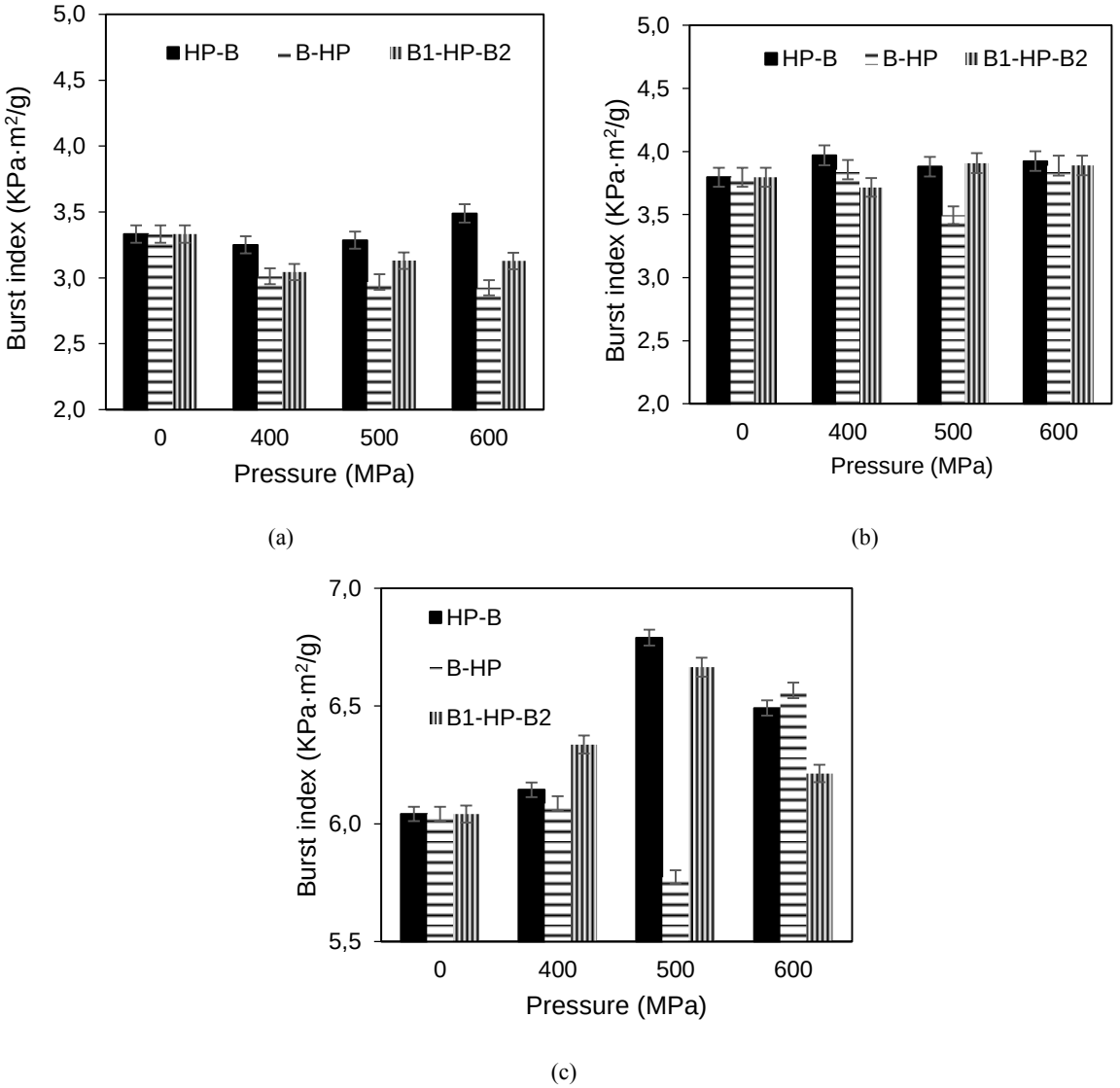


Figure 4. 12 - Burst index (KPa.m^2/g) of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

Tensile strength results of ***R*** samples series (Figure 4. 13a), were practically insignificantly affected by pressure in UHP step. However, in the case of ***E*** samples (Figure 4. 13b), for increased pressure conditions, a clear tendency of tensile strength increment was observed. The increment was notable when the beating stage followed the UHP treatment. This was manifested in HP-B and B1-HP-B2 sequences. This fact indicates that UHP promotes the defibration in forthcoming beating operation. Such assumption is also valid when UHP is applied intercalary in beating sequence. In the case of ***S*** fibres series, the variations in strength were the most significant. The beating applied

after the UHP stage at 500MPa allowed almost 17% increase in strength of pulp (Figure 4. 13c).

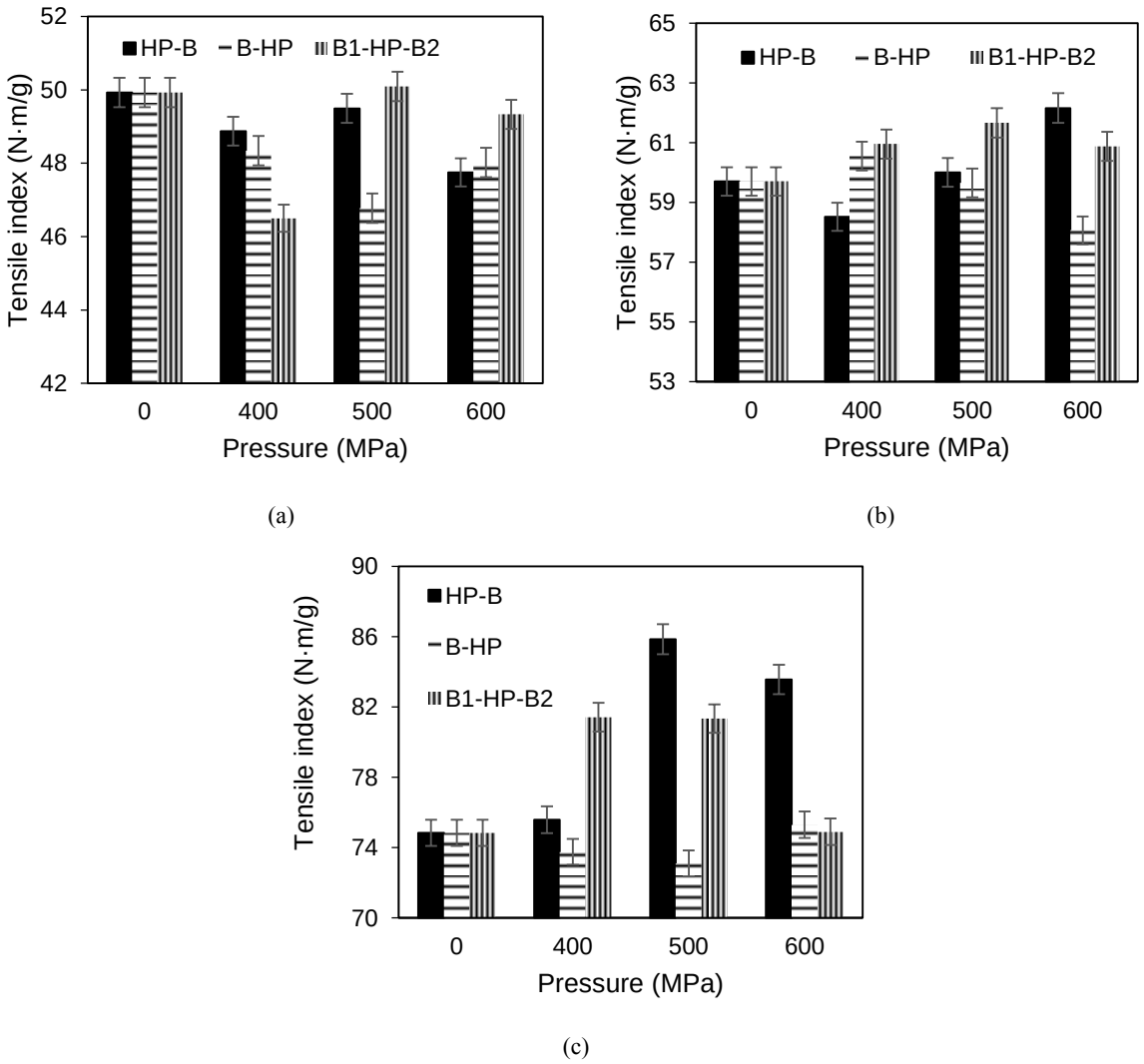


Figure 4. 13 - Tensile index of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

The increase of pressure in UHP processing of all kind of fibres (pulps ***R***, ***E*** and ***S***) within all beating sequences led to the sustainable increase in stretch (Figure 4. 14). This fact may be explained by the enhanced forced hydration of pulp fibres, making them elastic, thus increasing the handsheet deformation to ultimate tensile.

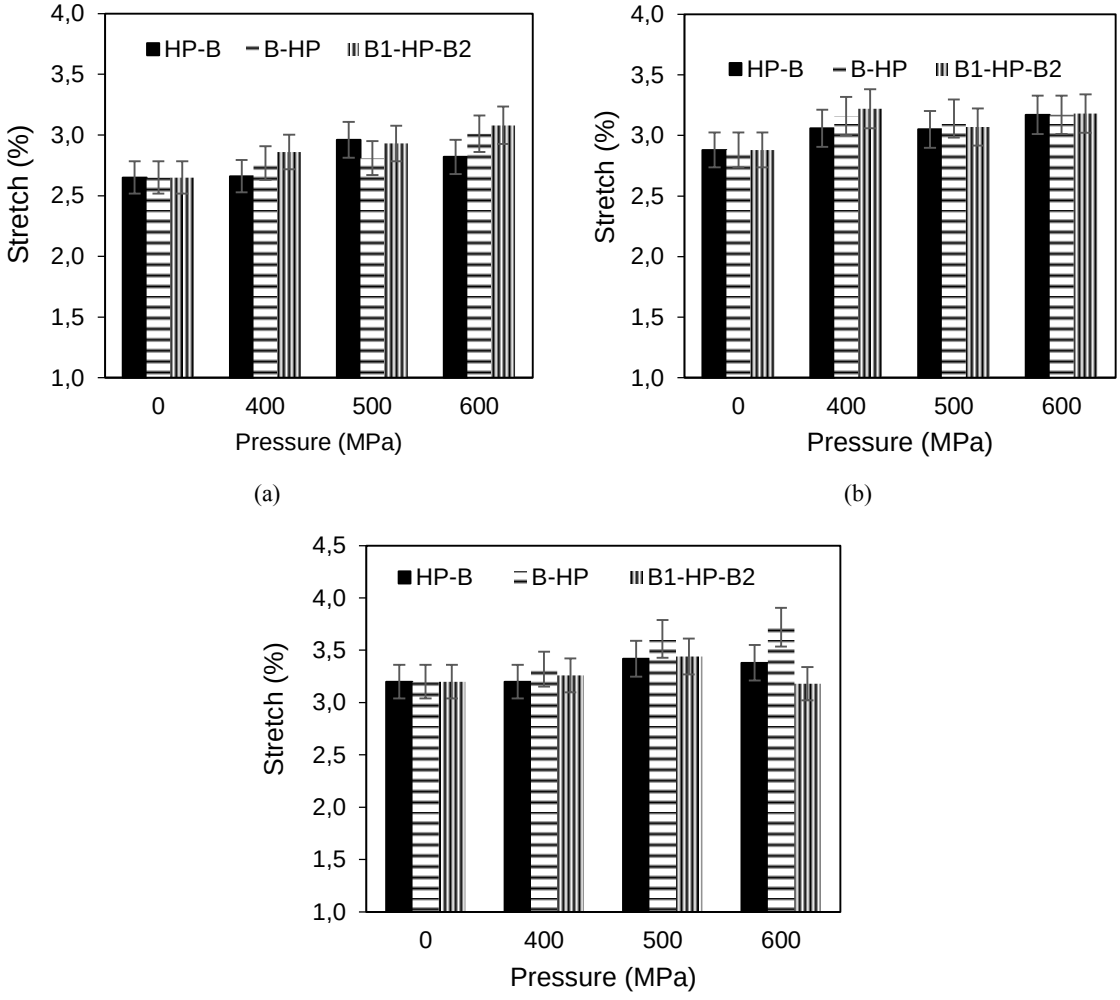


Figure 4. 14 - Stretch % of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

Results on tear index from recycled fibres (***R*** samples series), and its values are depicted in Figure 4. 15a. In fact, no significant changes were found within the range of pressures used in different heating sequences containing UHP stages. This result is similar to burst and strength characteristics discussed before (Figures 4. 12 and 4. 13). This fact may be explained by the fact that paper network improvements gained, by implementing UHP treatment, were minimized by the frailer structure of recycled fibres that limited its intrinsic properties.

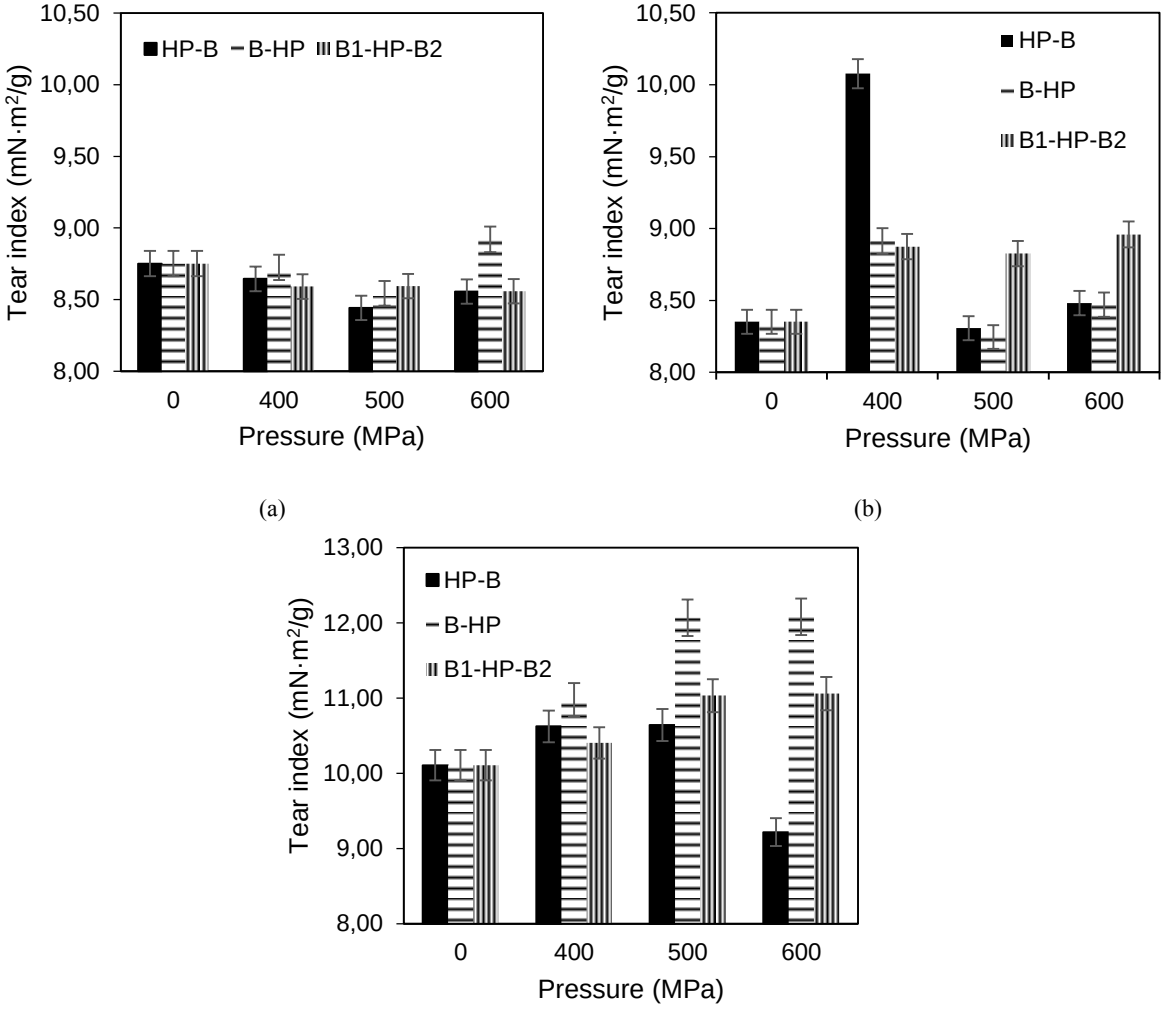


Figure 4. 15 – Tear index (mN.m^2/g) of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

In contrast to recycled fibres, virgin ones demonstrated improvements in tear resistance while increasing the processing pressure in UHP stages (Figure 4. 15), thought these improvements were not so straightforward. Thus, ***E*** samples series (Figure 4. 15b), showed a decrease of tear resistance in HP-B and B-HP sequences and similar values in the range of 400-600 MPa. In contrast, softwood fibres series, ***S***, displayed higher tear values, while increasing the pressure from 400 to 600 MPa in UHP stage, with exception of 600 MPa for HP-B (Figure 4. 15c). The different trend displayed by softwood fibres, relatively to the other fibres, could be attributed to softwood fibres dimensions (long fibres) and morphologies. In this case the synergetic effect of UHP treatment and beating may have contributed sharply to improve inter-fibres bonding.

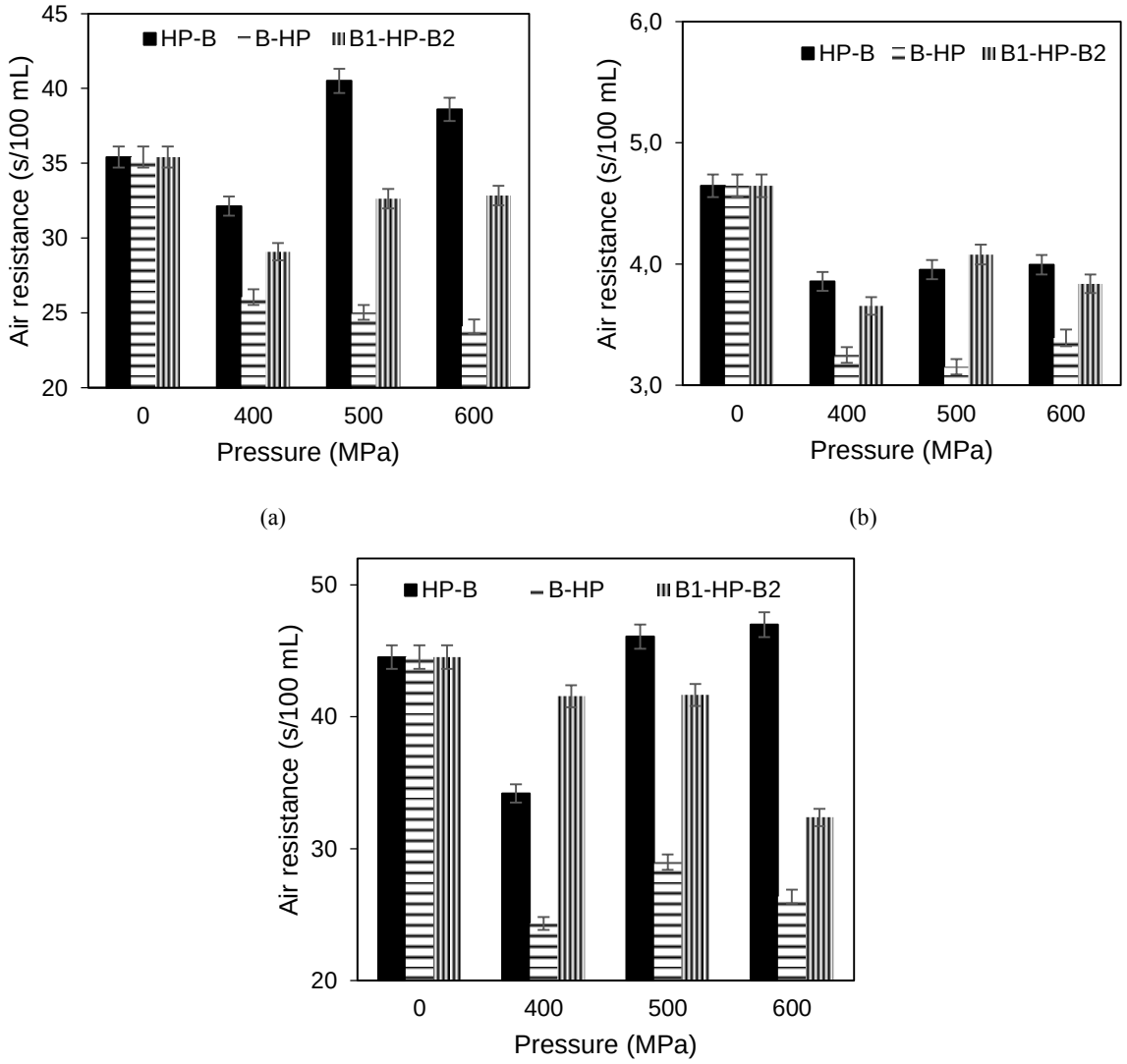


Figure 4. 16 - Air Resistance (s/100 mL) of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

Gurley's air resistance data for ***R*** samples series are presented in Figure 4. 16a. In general, air resistance increased, while increasing the pressure in UHP stage. The exception was detected with B-HP sequence only, which showed a decrease in air resistance, in the pressures range of 400-600MPa. The low air resistance values presume a porous handsheet and thus more free spaces between fibres. The increase of air resistance with increasing pressure in UHP stages, although not superior to untreated samples, reflects the fibres enlargement and, thus, the appearance of larger spaces between fibres in handsheets.

The decrease of air resistance was also found for virgin fibres, ***E*** and ***S*** series (Figures 4. 16b and c, respectively), with emphasis on sequences B1-HP-B2 and B-HP. It

is possible that in those cases increased UHP rendered higher fibres enlargement and thus handsheets with higher porosity and roughness.

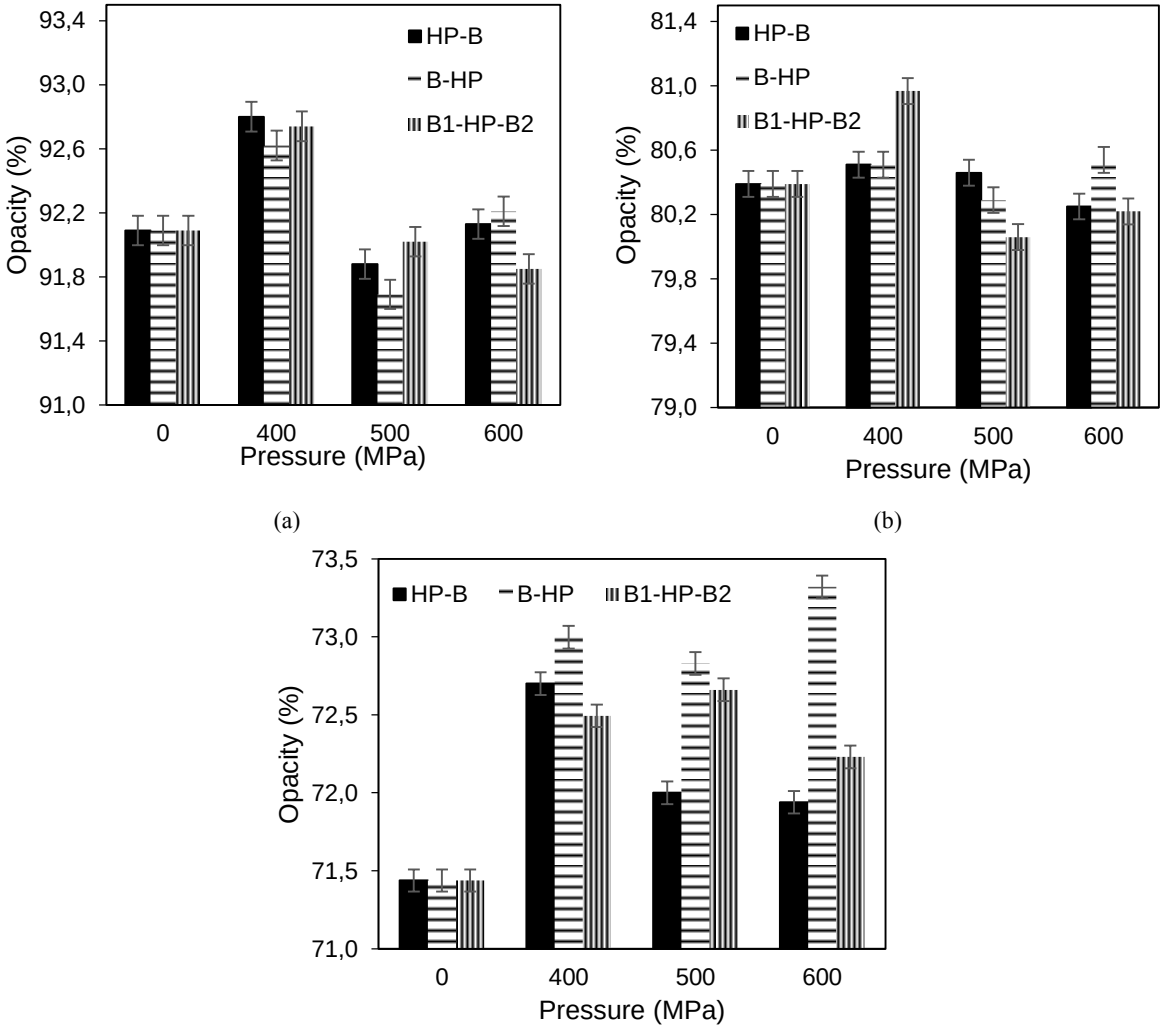


Figure 4. 17 - Opacity (%)of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

In the case of opacity (%) (Figure 4. 17), a decrease in recycled pulp treated by the beating sequences, with increasing of pressure in UHP stage, may be associated with some decrease of bulk (Figure 4. 11). Hardwood fibres, ***E***, series (Figure 4. 17b) displayed a similar behaviour, with lower opacities from 500MPa onwards. In case of softwood fibres (Figure 4. 17c) increased opacities were achieved in sequences B-HP and B1-HP-B2, where the UHP stage was applied after the beating step. The reverse dependence was found in HP-B sequence, which corroborates with bulk dependence from pressure in UHP stage, as discussed previously (Figure 4. 11).

Capillarity tests revealed almost continuous increase of water absorptivity with the increase of pressures in UHP stages. However, in the case of short fibres (***R*** and ***E***) capillarity increased insignificantly in the pressure range from 500 to 600 MPa, whereas in the case of long fibres the capillarity increment was still notable. It seems that the pressure of 500 MPa was the best from the point of view of pulp absorptivity for the recycled fibres.

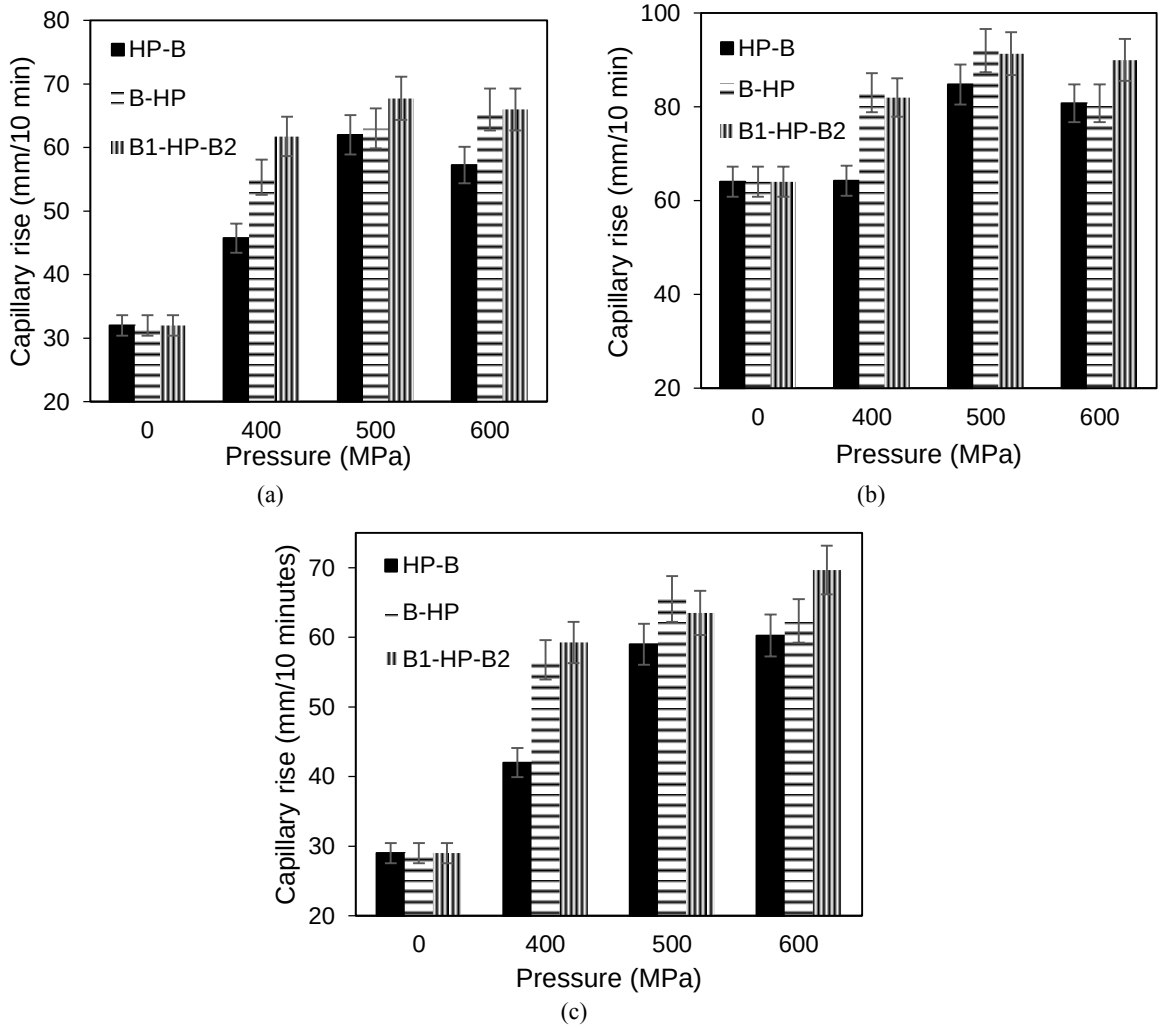


Figure 4. 18 – Capillary rise (mm/10min) of ***R*** samples (a), ***E*** samples (b) and ***S*** samples (c), upon treatment with sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions (***R***=1000 PFI revolutions, ***E***=3000 PFI revolutions and ***S***=6000 revolutions), as a function of pressure (0, 400, 500 and 600 MPa, 10 min).

The remarkable improvements found on the absorptivity of fibres hydration skill (Figure 4. 18) are the results of the synergetic effect of UHP (stronger for increased pressures) with beating. As previously mentioned, capillarity is influenced by fibres porosity, and according to Young-Laplace equation, by liquid-air surface tension, cosine of contact angle and the inverse of capillaries radium. Therefore, in the formed handsheets, considering these facts and the improvement of porosity and hydrophilicity, as result of

UHP treatment, it is probable that together these might have contributed to improve handsheets absorptivity, especially upon higher pressures (stronger UHP effect).

4.3.5.2. Fibre morphology analysis

The effect of different pressures in UHP treatment on fibres morphologies was performed at pressure values ranging from 400 to 600 MPa, at fixed beating conditions (at 1000 PFI revolutions for ***R***, at 3000 PFI revolutions for ***E*** and at 6000 PFI revolutions for ***S***). The data for recycled fibres is displayed in Table 4. 4, while virgin fibres results are shown in Table 4. 5.

For the pressures as high as 400 MPa, no decrease in fibres length was detected in any beating sequence conjugated with UHP steps. This means that internal and external fibrillation were predominant over shortening. Such result may be due to improved fibres hydration, with increased pressure in UHP treatment that affected the plasticity of fibres, thus becoming less prone to shortening. Coarseness of fibres was clearly decreased, while increasing the pressure in UHP stage, in all beating sequences, indicating an improve fibre wall fibrillation/dilapidation. The mean kin index values were either similar to those of 400 MPa or higher, suggesting enhanced fibres deformation, possibly resultant from a decreased coarseness.

Table 4. 4 - Fibres characteristics, for non-treated ***R*** pulps and ***R*** pulps subjected to beating sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions and at different pressures in UHP stage (400, 500 and 600 MPa).

R	Without HP	400 MPa			500 MPa			600 MPa		
	R	HP-B	B-HP	B1-HP-B2	HP-B	B-HP	B1-HP-B2	HP-B	B-HP	B1-HP-B2
Length (mm) ±0.04	0.86	0.86	0.86	0.82	0.84	0.84	0.85	0.85	0.85	0.85
Coarseness (µg/m) ± 9	146.5	189.3	187.6	132.3	146.9	149.5	122.0	120.4	173.6	110.4
Mean kink index ±0.13	2.65	1.87	1.90	2.53	2.58	2.06	2.63	2.46	1.80	2.05

As concerns virgin fibres, ***E*** and ***S***, series (Table 4. 5), its length was not substantially affected in beating sequences, with increasing pressure (over 400 MPa). This result is in agreement with an intact fibre walls in virgin pulps, in opposite to recycled fibres (damaged and previously beaten fibres). In the case of ***E*** samples, no changes in coarseness were observed with an increase of pressures in UHP stages. As a rule, mean kink index was decreased in sequences with the UHP stage after beating (B-HP and B1-HP-B2), when pressures raised from 400 to 600 MPa.

Similar tendencies, as with hardwood pulp ***E***, were obtained with softwood pulp, ***S***, (Table 4. 5), thought the decrease of mean kink index was observed only after B-HP sequence in the pressure range of 400-600 MPa.

The differences in coarseness dependences in different beating sequences of recycled (***R***) and similar by nature virgin (***E***) pulp may be assigned to fibres morphologies. Thus, recycled fibres are strongly damaged and practically have no primary cell wall, whereas virgin fibres possess an intact cell wall. This fact predetermines the easier expansion of secondary wall in ***R*** than in ***E***. Hence, mechanical peeling of the formers is relatively fast. This explains the coarseness decrease in ***R*** with increased pressures in UHP stage and it low variation with pressure in ***E***.

Table 4. 5 - Fibres characteristics, for non-treated virgin pulps (***E*** and ***S***) and virgin fibres subjected to sequences HP-B, B-HP and B1-HP-B2, at fixed beating conditions and at different pressures in UHP stage (400, 500 and 600 MPa).

E	Without HP	400 MPa			500 MPa			600 MPa		
	E	HP-B	B-HP	B1-HP-B2	HP-B	B-HP	B1-HP-B2	HP-B	B-HP	B1-HP-B2
Length (mm) ±0.03	0.75	0.75	0.75	0.76	0.75	0.75	0.75	0.74	0.75	0.76
Coarseness (μg/m) ±5	84,6	86,5	85,1	83,3	80,5	84,2	82,1	89,5	87,1	89,5
Mean kink index ±0.12	2,26	2,50	1,93	2,22	2,30	1,76	2,19	2,34	1,79	0,98
S	Without HP	400MPa			500MPa			600MPa		
	S	HP-B	B-HP	B1-HP-B2	HP-B	B-HP	B1-HP-B2	HP-B	B-HP	B1-HP-B2
Length (mm) ±0.08	1.78	1.79	1.79	1.78	1.78	1.77	1.84	1.77	1.79	1.77
Coarseness (μg/m) ±10	181.3	192.7	193.1	180.3	176.4	189.8	193.7	178.6	194.1	185.0
Mean kink index ±0.12	1.73	2.29	1.49	2.28	2.32	1.55	2.04	2.38	1.45	2.41

4.4. Conclusions

The results of this study revealed the effect of UHP treatment on papermaking properties of both recycled (***R***) and virgin hardwood (***E***) and softwood (***S***) pulps. The forced hydration of fibres upon UHP treatment, in general, favours the defibration in subsequent beating stages, which, however, was not necessary reflected by the formal increasing of beating degree (ºSR). This was particularly notable when UHP stage was applied after the beating stage (B-HP sequence). Recycled pulp showed the highest increase in formally determined pulp beatability (up to twice) in the B1-HP-B2 beating sequence (pre-beating followed by UHP step and posterior beating stage). These improvements in beating were fairly moderated in the case of virgin pulps (***E*** and ***S***). The increase of pressure in UHP treatment from 400 to 500 or 600 MPa led to the acceleration of beating in the case of recycled fibres, especially in the HP-B sequence (UHP pre-treatment stage followed by beating), and to moderate or negligible beating improvement in the case of virgin pulps. The observed differences in UHP effect of beating behaviour for recycled and virgin fibre were explained by different fibre morphologies (intact or degraded primary cell walls).

The improved beating of both recycled and virgin fibres was not always transformed into the improvement of strength properties of refined pulps. This fact was related to the forced hydration of fibres leading to their increased elasticity and some decreased bonding capacity, due to the smaller overlapping of fibres (less interfibrillar surface) and diminished amount of free groups (part of OH groups are involved in water clathrates). Physical properties were improved to some extent, while increasing the hydraulic pressure in UHP treatment from 400 to 500 or 600 MPa. The improvements depended from pulp origin and were minimal for recycled pulp and maximal for virgin softwood pulp (from 10 to 20%). Optimal pressures in UHP step depended of pulp origins and beating sequences applied.

The combination of UHP treatment and beating in various combinations allowed improvements of pulp handsheets opacity and capillarity. The highest improvement of capillarity was found for recycled and virgin softwood pulps, (more than twice), which was always enhanced by increasing of pressure in UHP stage.

It may be also concluded that the best desired properties of papers will be dependent on pulps origin and the beating sequence applied under particularly optimised conditions. Overall, UHP treatment may be an interesting tool to improve recycled and virgin pulps performance in the production of tissue papers.

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Chapter V

Effect of ultra-high pressure on enzymatic modification of recycled pulp

Contents

5.1. Introduction

The production of recycled paper has grown all over the world.[1,2] This increase was essentially driven by political issues, consumer's demands and environmental awareness. Nowadays nearly 30-50% of cellulosic fibres are recycled worldwide and its consumption offers several advantages. Its use in papermaking contributes to reducing the depletion of forest resources and to decrease energy and water consumption.[3–5] However, several disadvantages can still be associated with recycled paper. The main problems are related to (i) the feedstock variability, (ii) significant losses on fibres strength properties due to hornification, and (iii) the presence of impurities (such as inks, glues, stickies, etc.).[6,7] Yet, hornification is still considered the main responsible for the losses of recycled pulp strength properties. It occurs as results of the stressful conditions fibres are submitted, repeatedly, during their lifecycle (pressing and drying during paper production, re-pulping ageing, etc.). These factors contribute to irreversible changes in fibres structure, yielding its surface collapse, shrinkage, stiffening and limited swelling in water.[8–10] As result, recycled pulps strength decreases considerably, which limits its re-use in papermaking. In truth, it is almost impossible to use 100% recycled fibres in paper composition without the addition of a significant proportion of virgin pulp. Additionally, the number of re-using cycles of recycled pulp is limited to 3-5.[3–5] In order to improve recycled fibres performance, different approaches may be followed, being the most conventional chemical treatments (swelling with alkaline solutions) and reactive refining (beating with enzymes aid or some inorganic bases/salts) in water. [6,8,11–13]

Enzymes have been recognised as an environmentally friendly solution in fibre modification. These act selectively on fibres constituents, improving its strength properties and promoting the inter-fibre bonding in paper.[14,15] In what concerns recycled fibres, its treatment with some hydrolytic enzymes enables improved removal of ink and other impurities, while retaining fibres properties, as much as possible.[16] Enzymes such as cellulases, hemicellulases, amylases, and lipases could be used separately or in conjunction, depending on the type of waste paper and impurities, to optimize the purification process. Generally, enzymatic treatment occurs either by attacking the ink or the fibre surface on the fibre-ink interface. Thus, lipases and esterases degrade vegetable oil-based inks, while pectinases, hemicellulases, cellulases and ligninolytic enzymes alter the fibre surface or the bond close to ink particles, hence releasing ink for removal.[7,14,17]

Xylan is a major hemicellulose in hardwood pulps, which can be selectively depolymerized by xylanase. This property was successfully used for both hardwood kraft pulps bleaching or upgrading to dissolving pulps.[15,18,19] By breaking the covalent linkages between xylose residues, xylanase is able to hydrolyse xylan into leachable oligosaccharides. The removal of xylan oligosaccharides, together with substituted hemicelluloses and covalently linked lignin, from the fibre surface, results in improved bleaching, also due to the enhanced penetration of bleaching agents. [20,21] The use of xylanases for the treatment of recycled pulps is much less studied than with other enzymatic systems.[14]

Ultra-high hydrostatic pressure (UHP) treatment is a relatively new technique, which has demonstrated the ability to reverse the limitations laid on recycled fibres by hornification due to forced hydration and introduction of strongly bound water in pulp.[22] UHP treatment prompts rearrangements to the fibre structure, which increase accessibility towards chemicals and enzymes.[22–24]

Considering the aforementioned, the main goal of this study was to evaluate the effect of selective modification of recycled pulp by xylanase, also promoted by UHP pre-treatment, on the strength properties of recycled pulp. It is noteworthy that the studies described in this chapter were published and are thus available for viewing in a journal article entitled “High pressure-promoted xylanase treatment to enhance papermaking properties of recycled pulp”.[25]

5.2. Materials and Methods

Recycled pulp, ***R***, and *eucalyptus globulus* bleached *kraft* industrial pulp, ***E***, (from the same lots used in the previous chapters) were kindly supplied by Renova FPA, S.A. and used on the studies performed on this chapter. The enzyme applied in pulp treatments was commercial *endo*-β-1,4-xylanase (E.C.# 3.2.1.4; enzyme activity of 2.5 AUX/mg) from *Thermomyces lanuginosus* (X2753 from Novozymes Basionics®).

5.2.1. Neutral sugar analysis

Neutral sugar analysis was performed following the same methodology described in ***Chapter 3***, section **3.2.1.7**.

5.2.2. Hydrostatic ultra high-pressure treatment (UHP)

Pulp dispersions (2% consistency) of ***R*** or ***E***, were prepared with sodium acetate buffer solution (0.05 M sodium acetate buffer at pH 5) and placed into HDPE flasks. Afterwards, the flasks containing the pulp dispersions were subjected to UHP treatment, at different pressure conditions (300, 400, 500 and 600 MPa, for 10 min) on a high-pressure apparatus, model 55 Hyperbaric (Burgos, Spain), under aqueous medium.

5.2.3. Enzymatic hydrolysis

- Sodium acetate hydrate (99%, Panreac)
- Glacial Acetic acid (99.7%, Fluka)
- Distilled water

The enzymatic hydrolysis was performed according to the following procedure, 1g of dry pulp was dispersed in 50 ml of 0.05 M sodium acetate buffer. In the case of UHP treated samples, after UHP those were diluted up for 50 mL. Afterwards, pulp dispersions were placed in a round-bottom flask, under stirring, at 40 ºC. A suspension of enzyme (0.5 ml of a 4 mg/ml solution, 5 AUX/g pulp), prepared in advance, was them added to the stirring pulp dispersion and allowed to react for 75 min. Aliquots for reducing sugars (RS) analysis were collected at 2, 5, 10, 15, 30, 45, 60 and 75 min and analysed using 3,5-dinitrosalicilic acid (DNS) method.[26] The pulp samples used to produce paper sheets were treated under the same conditions and enzymatic load.

5.2.4. Reducing sugar quantification (DNS method)

- 3,5 – Dinitrosalicylic acid, DNS (98%, Merk)
- NaOH (97%, Acros Organic)
- Potassium sodium tartrate (99%, Acros Organics)
- Glucose (99%, Sigma-Aldrich)
- Distilled water

The DNS method[26] was used to monitor the amount of RS released during the enzymatic reaction. Firstly, the DNS reactant was prepared. To do it a 2 M NaOH solution was prepared by dissolving 8 g of NaOH on 100 ml of water, under stirring and heating. At the same time, a solution of potassium sodium tartrate was prepared by dissolving 150 g of this reactant with 250 ml of distilled water. When the NaOH solution (under stirring and heating) reached approximately 100 ºC, 5 g of DNS were added. Afterwards, when the mixture approached approximately 60 ºC, the tartrate solution was added. The mixture was left stirring until all DNS was dissolved. Then it was cooled down and stored.

To quantify the produced RS, 0.5 mL of a filtered aliquot (in duplicate), collected during the enzymatic reactions, was added into o soviril tube. After adding 1 ml of DNS, the tube was closed and placed under boiling water (100 ºC) for 5 min. The sample was then placed on ice to cool down and diluted by adding 10 ml of distilled water.

The quantification was carried out on a UV-Vis spectrophotometer, Evolution 220 from Thermo Scientific at 540 nm. To all absorbance values, it was subtracted the value of the blank, which consisted of buffer solution subjected to the same procedure of samples.

The calibration curve for RS quantification was performed by applying the described method to glucose standard solutions of 0.2, 0.4, 0.8, 1, 2 and 3 mg/mL of concentration. From their absorbance values and concentration values, a calibration curve was achieved and is presented in Appendices C.

5.2.5. Handsheets formation

To evaluate the physical and mechanical properties of pulp samples, handsheets were prepared following ISO 5269-2:2004, on a Rapid- Köthen sheet former (Karl Schröder KG).

5.2.6. Physical and mechanical properties evaluation

Fibres drainability was evaluated by analysing the *Schopper-Riegler* degree according to ISO 5267-1:1999. Thickness, density and specific volume of prepared

handsheets (section **5.2.5.**) were evaluated according to ISO 534:2011. Tensile strength, stretch, tear index, burst index, air resistance (Gurley method) were evaluated following ISO 1924-2:2008, ISO 1974:2012, ISO 2758:2014 and ISO 5636-5:2013, respectively. Brightness and fluorescence of hand sheets were determined following ISO 2470-1:2009, using an Elrepho brightness tester (Lorentzen & Wettre). Water retention value (WRV) was determined by centrifuge method based on a procedure developed by Jayme (1958).[27]

5.2.7. Xylan removal yield

The xylan removal yield was monitored considering changes on the neutral sugar contents (shifts on xylose content) and the weight loss registered for each sample after each treatment.

Variations on mass were also followed. With this purpose a microporous filter (no.3) was weighted before the reaction, then it was used to filter the reaction medium and, after dried along with the filtrate at 105 ºC (until 0% HR), was weighted again.

The formula used to calculate the yield is given by equation 4.1.

$$Yield\ (\%) = \frac{(100 - Weight\ loss(\%)_{sample}) * xylose\ fraction_{sample}}{Xylose\ percentage\ on\ the\ non\ treated\ pulp} \qquad \text{Equation 4. 1}$$

5.2.8. Scanning electron microscopy (SEM)

Pulp samples were also analysed through scanning electron microscopy (SEM), on a Hitachi S4100 equipment at 15 kV. Each sample was attached to a SEM support with carbon tape, then subjected to Au/Pd sputtering before analysis.

5.3. Results and Discussion

The effect of UHP on xylanase hydrolysis and modification of recycled fibres, ***R***, was studied. Since chemical analysis (***Chapter 3,*** section **3.3.1.**) showed similarities between the chemical composition of the selected recycled fibres (***R***) and virgin eucalypt pulp (***E***), this last may simulate pulp ***R***, before its involvement in the papermaking process. Hence, ***E*** pulp was used here as non-processed virgin fibres for comparative reasons.

5.3.1. Effect of UHP pre-treatment on the enzymatic treatment of pulp

5.3.1.1. Reducing sugars release

E and ***R*** samples were subjected to UHP pre-treatment under different conditions (0, 300, 400, 500 and 600 MPa, during 10 min) and, after that, were treated with xylanase at 40ºC during 75 min. The removal of xylan, by enzymatic hydrolysis, was monitored by the release of reducing sugars (RS), according to the DNS method.[26] The RS release profiles are displayed in Figure 5. 1 (recycled fibres) and Figure 5. 2 (virgin fibres). For simplicity, each sample was labelled as described below. ***R*** consists of recycled fibres sample, without UHP pre-treatment and subjected to enzymatic treatment. The other recycled fibres samples of recycled fibres subjected to UHP pre-treatment and enzymatic hydrolysis, were labelled as *"**RXXX**"*, where *"**XXX**"* corresponds to the pressure applied during the UHP pre-treatment (300, 400, 500 or 600MPa). The same labelling method was used for virgin fibres, being ***E*** the pulp sample without UHP pre-treatment and subjected to enzymatic treatment, while *"**EXXX**"* samples consist of pulp samples subjected to both UHP pre-treatment and enzymatic hydrolysis.

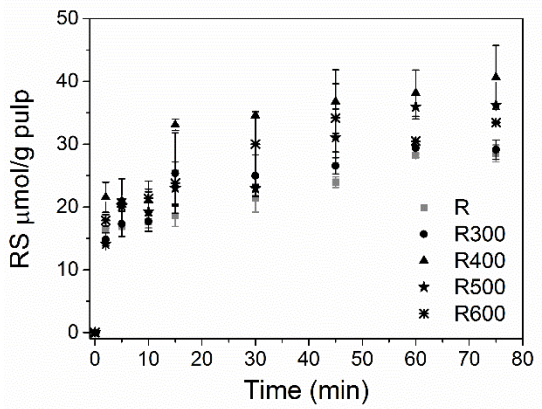

Figure 5. 1 – Reducing sugars (RS) release as a function of time for recycled pulp (***R***) subjected to xylanase hydrolysis after the UHP treatment at 300MPa (***R300***), 400MPa (***R400***), 500MPa (***R500***) and 600MPa (***R600***).

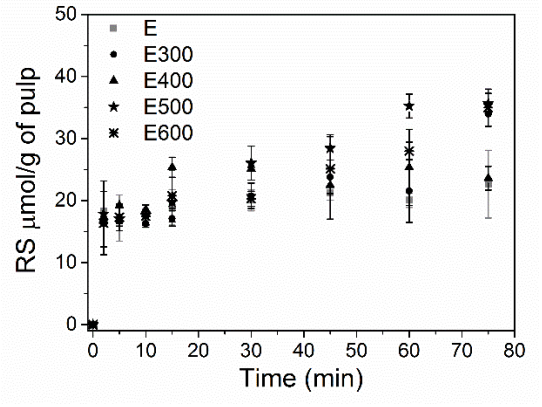

Figure 5. 2 – Reducing sugars (RS) release as a function of time for virgin pulp (***E***) subjected to xylanase hydrolysis after the UHP pre-treatment at 300MPa (***E300***), 400MPa (***E400***), 500MPa (***E500***) and 600MPa (***E600***).

In both types of fibres (recycled and virgin fibres), the increase of RS release was observed for samples subjected to UHP pre-treatment, with a sudden rise at ca. 10min. In opposite, pulps not treated by UHP revealed a slower and continuous release of RS. Furthermore, it was found that RS release profiles depended on the pressure conditions applied.

As regards ***R*** (without UHP pre-treatment), this sample released the lowest RS, upon enzymatic hydrolysis, followed by ***R300*** (recycled fibres treated at 300MPa). Even though ***R500*** (recycled fibres treated at 500MPa) and ***R600*** (recycled fibres treated at 600MPa) also exhibited a higher RS release, when compared with ***R*** and ***R300***, it was ***R400*** (recycled fibres treated with 400MPa) the one displaying the highest RS release (Figure 5. 1). Thus, as showed by RS release, xylan partial removal was promoted by UHP pre-treatment.

Xylan removal was particularly fast during the first 2min of enzymatic hydrolysis, then further xylan removal from fibre cell wall occurred slowly, especially for pulp fibres untreated by UHP (***R***). These features can be explained by the easy hydrolysis of xylan from fibres surface, whereas the accessibility of interior layer in fibres was significantly reduced. Nevertheless, even recycled pulp untreated by UHP, ***R***, demonstrated a weak growth of RS release till 60min of enzymatic hydrolysis. This fact may be explained by the improved accessibility of beaten ***R***, already used in papermaking, due to the mechanical damage/defibration of the fibre cell wall.

In the case of virgin hardwood fibres, used for comparative reasons, samples subjected to UHP pre-treatment also revealed an increase of RS release, though maximum RS concentrations in hydrolysates were registered after 500MPa pre-treatment and not after 400MPa, as in the case of recycled fibres (Figure 5. 2). The maximum rate of xylan removal was associated with the maximum efficiency of enzyme promoted fibre modification, with respect to surface purification and accessibility. Xylan removal from ***E*** (monitored by RS release) was stagnant after 10min of enzymatic hydrolysis, possibly due to hindered accessibility to intact cell wall if virgin fibres (unbeaten fibres).

Although, in both cases, recycled and virgin pulps showed an improved accessibility to xylanase, after the UHP pre-treatment, the maximum xylan removal was observed for ***R*** and ***E***, under different hydrostatic pressures. Thus, the highest xylan hydrolysis for ***R*** was observed after UHP pre-treatment at 400MPa and at 500MPa for ***E***. The UHP treatment leads to forced hydration of cellulosic fibrils in the pulp and to the disaggregation of

microfibrils (bundle of fibrils), thus opening the inter-microfibrillar space for enzymatic attack on the xylan that envelops the cellulose microfibril (Figure 5. 3).[24]

Along the UHP pre-treatment in time or when increasing the hydrostatic pressure, the forced hydration of fibrils inside cellulose microfibrils proceeds, thus decreasing the space between microfibrils due to its enlargement. As a consequence, the accessibility of xylan in inter-microfibrillar space is diminishing. Apparently, the partially disintegrated cell wall of ***R*** fibres requires less severe hydrostatic pressure to disaggregate cellulose microfibrils than the intact cell wall of ***E*** fibres.

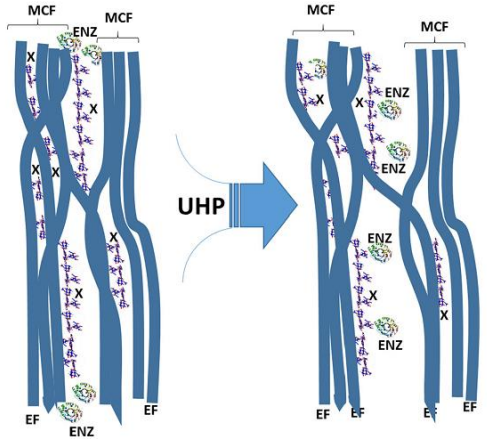

Figure 5. 3 - Schematic representation of the effect of ultra-high hydrostatic pressure (UHP) treatment on the improvement of fibre cell wall accessibility towards xylanase (ENZ). Forced hydration favours the disaggregation of microfibrils (MCF) and elementary fibrils (EF), thus improving the accessibility of xylan (X) in the inter-microfibrillar space.

It was also suggested that the presence of cellulases in the supplied xylanases was insignificant because no decrease was found in the intrinsic viscosity of pulp, after the enzymatic treatment. In contrast, a small increase it was found from 925cm^3/g (***Chapter 3***, Table 3.3) to 940cm^3/g, due to partial elimination of relatively low molecular weight xylan.

5.3.1.2. Physical/Mechanical properties

Considering the optimum UHP treatment conditions for cellulosic pulps, ***R*** (400MPa) and ***E*** (500MPa), hand sheets from its corresponding pulps were prepared to evaluate the effect of the combination of UHP pre-treatment and enzymatic treatment (***R400E*** and ***E500E***, respectively). Additionally, for comparison both pulp without any treatment (***R*** and ***E***) and those treated solely with enzymes (***RE*** and ***EE***, respectively) or solely pre-treated by UHP treatment (***RHP*** and ***EHP***) were also considered (Table 5. 1 and 5.2).

Table 5. 1- Mechanical properties of the recycled fibres (***R***) upon enzymatic and high pressure treatments.

Samples	R	RHP	Δ (%)	RE	Δ (%)	R400E	Δ (%)
Brightness ISO %, (±0.1)	82.8	-	-	81.1	-2.1	80.7	-2.6
Fluorescence R 457 %, (±0.2)	10.1	-	-	9.2	-9.3	7.6	-25.1
°SR, (±0.5)	25	26	+4	38	+52.0	38	+52.0
WRV, % (±2)	82	83	+1.2	74	-9.8	78	-4.9
Bulk (cm^3/g), (±0.01)	2.16	2.14	-0.9	2.08	-3.7	2.04	-5.6
Burst index ($KPa.m^2/g$), (±0.05)	1.36	1.50	+10.3	1.68	+23.5	1.80	+32.4
Tensile strength (N m/g), (±0.50)	20.5	21.5	+4.8	23.7	+15.6	27.0	+31.6
Stretch (%) (±0.12)	2.46	2.76	+12.2	2.85	+15.9	2.76	+12.2
Tear index ($mN\ m^2/g$), (±0.25)	7.55	7.67	+1.6	7.59	+0.53	8.37	+10.9
Gurley's air resistance (s/100ml) (±0.10)	2.23	2.21	-0.9	4.74	+112.6	5.11	+129.1

* The variation (Δ%) of each property was determined with respect to the parent pulp ***R***.

Overall, xylanase treatment enhanced strength properties of recycled pulp (Table 5. 1). In the case of recycled fibres solely treated with xylanase (***RE***), most of the physical properties were improved, which were further boosted upon UHP treatment (***R400E***). Although UHP pre-treatment itself did not improve significantly the physical properties of ***R*** (***RHP***), UHP certainly had a synergistic effect on those properties when combined with posterior enzymatic treatment. This is especially notable for tensile strength and the tear resistance, as evidenced from analyses on ***RE*** and ***R400E***, which were improved up to 30%. The air resistance was also superior for enzyme-treated pulp demonstrating paper structure closure due to improved fibre-fibre interaction. Such features may be related both to the enhanced accessibility of ***R*** fibres towards xylanase and by forced hydration and favourable rearrangement of cellulosic fibrils in fibres after UHP pre-treatment. As it was previously suggested, UHP treatment leads to disaggregation of fibrils by forced hydration of their surface and to rearrangements of cellulose fibrils, leading to crystallite aggregation and diminishing of the distortion of their surfaces.[22] All these changes promote the fibre bonding capacity and increased intrinsic fibre strength. UHP treatment of cellulosic fibres also leads to the increase of strongly bound water in pulp, thus diminishing its susceptibility to hornification.[22]

The significantly increased drainability of enzyme-modified pulp (***RE***) evidenced for the improved swelling capacity of recycled pulp, though this was not accompanied by the increasing of WRVs due to the removal of hydrophilic xylan from pulp. It is suggested that

the partial removal of xylan, bound to impurities and to cellulose fibrils, on the surface of recycled pulp, would favour the ensuing swelling and inter-fibre bonding of purified ***R*** fibres in handsheets. This is a reason for the notable improvement of mechanical properties of ***R***, after the enzymatic treatment (Table 5. 1). The increased drainability, after the enzymatic treatment, indicates that ***RE*** might possess much better refinability than the initial ***R*** (Table 5. 1). This is an attractive point for economic manufacture of paper from recycled fibres since the energy costs for pulp refining are the main expensive item of paper production.

In contrast to strength parameters, a small decrease in recycled pulp brightness was observed after enzymatic treatment. These features are also demonstrated by reflectance spectra of paper sheets in the range of 200-450nm (Figure 5. 4). The decrease in recycled pulp reflection at 475nm was correlated with the loss of calcium carbonate filler, under weakly acidic conditions, after the enzymatic treatments. In parallel tests it was observed that when pulp ***R*** was treated solely with buffer (pH 5), the reflection at 475nm would decrease nearly 1.2%. From the other side, the decrease in ***R*** brightness after enzymatic treatment may also be explained by the eventual removal of optical brightening agents (OBAs) present in printing papers. This fact was evidenced by the detected decrease in fluorescence R457 of the treated recycled pulp (Table 5. 1). The removal of OBAs is a typical feature for recycled pulps modified by enzymatic treatment.[28,29] However, the unexpected increase of *K/S* in the UV-vis DR spectra range of 220-350nm from ***R*** to ***RE*** and further to ***R400E*** (Figure 5. 4) was possibly the result of detachment of impurities (printing inks, auxiliary resins, etc) not only from the surface but also from the bulk of fibres, which under the treatment conditions, formed small dispersed particles that re-adsorbed further on fibre surface. Such explanation was suggested in previous studies on the enzymatically promoted deinking of recycled pulps.[29,30] According to literature,[30] the enzymatic treatment of alkaline paper (formed at pH 8-9) under weak acidic conditions, usually leads to the appearance of floating microparticles of toner/ink liberated as the result of its release from degraded calcium carbonate particles and inaccessible fibre surface. These ink microparticles tend to re-precipitate on fibres in the absence of appropriate surfactants, thus decreasing the pulp brightness. Apparently, forced hydration of pulp upon UHP treatment facilitates not only the enzyme penetration inside the cellulosic fibres, but also the detachment of impurities from the surface. This explains the highest increase of *K/S* in the UV-vis DR spectrum of ***R400E***, which is in agreement with a more pronounced enzymatic accessibility of pulp, due to UHP pre-treatment (Figure 5. 1).

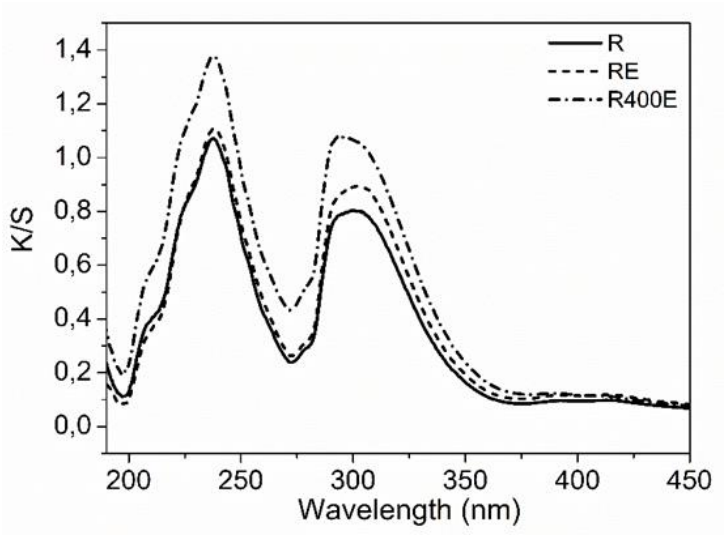

Figure 5. 4 – UV-vis reflectance spectra of handsheets prepared from recycled fibres (***R***), recycled fibres solely treated by enzymatic treatment (***RE***) and recycled fibres subjected to UHP pre-treatment and enzymatic treatment (***R400E***).

Table 5. 2 - Mechanical properties of virgin hardwood pulp (***E***) upon enzymatic and high pressure treatments.

Samples	E	EHP	Δ (%)	EE	Δ (%)	E500E	Δ (%)
Brightness ISO (%) (±0.1)	86.8	-		87.1	+0.3	87.2	+0.4
Fluorescence R457 %, (±0.05)	0.11	-	-	0.15	+36.4	0.13	+18.2
^{o}SR, (±0.5)	17	15	-11.8	17	0.0	17	0.0
WRV, % (±2)	62	61	-1.6	73	+17.7	72	+16.1
Bulk (cm^3/g), (±0.01)	2.06	2.14	+3.9	2.03	-1.5	2.00	-2.9
Burst index (KPa.m^2/g), (±0.03)	0.66	0.67	+1.5	0.84	+25.4	0.88	+31.3
Tensile strength (N m/g), (±0.4)	15.4	15.9	+3.2	18.30	+18.9	19.9	+29.4
Stretch (%) (±0.05)	0.79	0.74	-6.3	0.90	+13.9	0.93	+17.7
Tear index (mN m^2/g), (±0.15)	2.46	2.36	-4.1	3.40	+38.2	3.60	+46.3
Gurley's air resistance (s/100ml) (±0.05)	0.96	0.77	-19.8	1.16	+20.8	1.13	+17.7

*The variation (Δ%) of each property was determined with respect to the parent pulp ***E***.

For comparison, the same enzymatic treatment was also applied to ***E*** fibres (virgin hardwood fibres). Similar to ***R*** pulp, enzymatic treatment of pulp ***E*** led to a significant improvement of pulp strength properties being the most noticeable tensile strength and tear index. Again, it was found that pulp samples subjected to enzymatic treatment after UHP (***E500E***) exhibited much better results than those without UHP pre-treatment (***EE***). The relative improvement of strength properties for virgin pulp, observed after the UHP pre-treatment followed by enzymatic hydrolysis (***E500E***), was even higher than that for the recycled pulp after the same treatments (***R400E***). (Figure 5. 2). This can be explained, at

least partially, by the higher strength of virgin pulp fibres, comparatively to recycled ones, due to the less degraded pulp polysaccharides in the former. In fact, the intrinsic viscosity of ***E*** was almost twice to ***R*** (***Chapter*** 3, Table 3.3).

Nevertheless, in relative terms, UHP pre-treatment was more advantageous for pulp ***R***, than for pulp ***E***. At the same time, unlike pulp ***R***, UHP did not affect the drainability of pulp ***E*** (Table 5. 2). This may be explained, from one side by moderate enzymatic hydrolysis of virgin pulp and from the other side, by difficulties in swelling of fibres with intact primary cell walls.[31] Nevertheless, the WRV of ***E*** subjected to enzymatic treatment increased remarkably, thus indicating the enhanced internal swelling of pulp fibres. Also, in opposite to pulp ***R***, an enzymatic treatment of pulp ***E*** showed a small increase in pulp brightness (ca. 0.5% ISO) and no changes in fluorescence R457 (Table 5. 2).

5.3.1.3. SEM

The changes in pulp fibre morphology due to the enzymatic treatment, with and without UHP pre-treatment, were evaluated by image analysis using SEM. Figure 5. 5 displays the SEM images acquired from samples ***R***, ***RE*** and ***R400E***, while Figure 5. 6 exhibits the SEM images of samples ***E***, ***EE*** and ***E500E***.

The images of recycled fibres, ***R***, (Figure 5. 5a) exhibited damaged/defibrillated cell walls, which confirms that fibres from recycled pulp were previously beaten in papermaking, as proposed in section **5.3.1.1.**

The effect of xylanase on fibres can be observed when comparing ***R*** (Figure 5. 5a) with ***RE*** (Figure 5. 5b) and ***E*** (Figure 5. 6a) with ***EE*** (Figure 5. 6b). The external fibrillation of fibres induced by xylanase was visualised, as well as the diminishing of fibre surface collapse, especially for the recycled pulp. Visually, enzymatically treated fibres are better intertwined and possess higher contact areas than non-treated fibres. This becomes even more noticeable when comparing enzymatically modified fibres without (***RE*** and ***EE***) and with UHP pre-treatment (***R500E*** and ***E400E***) (Figure 5. 5c and Figure 5. 6c, respectively).

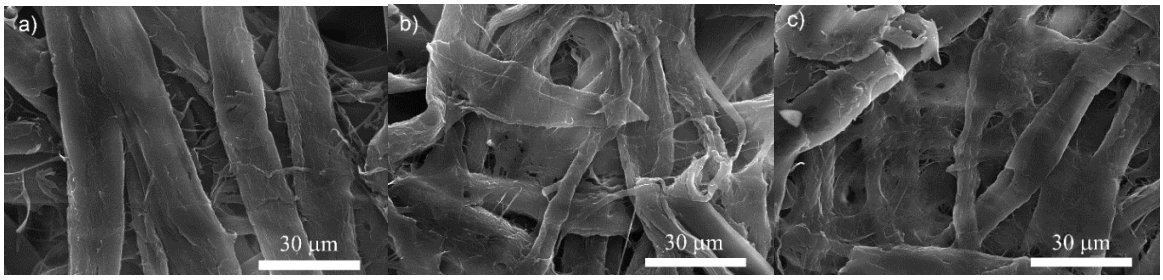

Figure 5. 5 - SEM image of recycled fibres, ***R***, (a); recycled fibres treated solely with xylanase, ***RE***, (b); and recycled fibres treated with UHP followed by xylanase treatment, ***R400E***, (c).

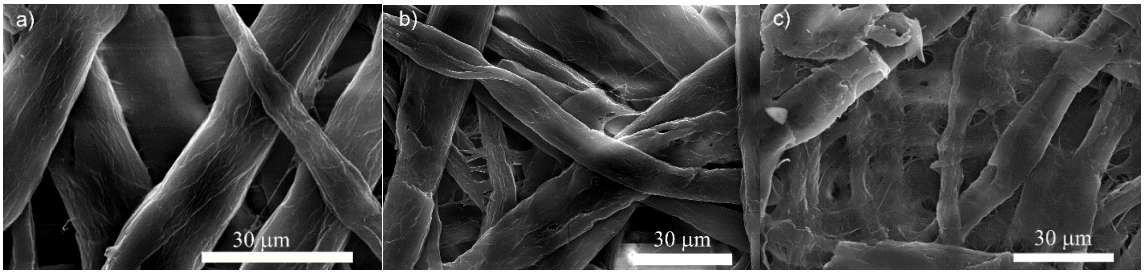

Figure 5. 6 - SEM image of *E. globulus* fibres, ***E***, (a); ***E*** fibres treated solely with xylanase, ***EE***, (b); and ***E*** fibres treated with UHP followed by xylanase treatment ***E500E***, (c).

5.3.1.4. Xylan removal yield

The extent of xylan removal from pulps upon xylanase treatment (from ***R*** to ***RE*** and ***R400E*** and from ***E*** to ***EE*** and ***E500E***) was also evaluated (Table 5. 4). In Table 5. 3 are presented the compositions of neutral sugars in the analysed samples, which were then used to determine the yield of xylan removal.

Table 5. 3– Neutral sugar composition of non-treated samples (***R*** and ***E***) samples treated solely with xylanase (***RE*** and ***EE***) and samples subjected to the combinations of UHP pre-treatment and xylanase treatment (***R400E*** and ***E500E***).

Samples	Arabinose %	Xylose %	Mannose %	Galactose %	Glucose %
R	-	22.8±0.1	-	-	77.2±0.1
RE	-	17.6±0.3	-	-	82.4±0.3
R400E	-	16.9±0.1	-	-	83.1±0.1
E	-	24.6±0.4	-	-	75.4±0.5
EE	-	22.3±0.4	-	-	77.7±0.4
E500E	-	21.6±0.3	-	-	78.4±0.3

Table 5. 4 – Yield of xylan removal on samples treated solely with xylanase (***EE*** and ***RE***) and samples treated with the combination of UHP pre-treatment and xylanase (***R400E*** and ***E500E***).

Samples	Yield (Xylan removal)%
RE	23.4±2.0
R400E	26.1±2.0
EE	10.1±0.6
E500E	12.2±0.6

In all cases, with both pulps, UHP pre-treatment boosted the extent of xylan enzymatic hydrolysis by 10-20% (***R400E*** and ***E500E***). The amount of xylan removed from the recycled pulp was roughly twice of that observed for the virgin pulp, which can be explained by the higher accessibility of the former, due to structural disintegration of fibres after beating during paper production and because of paper life cycle (e.g. abrasion, folding and ageing).

5.4. Conclusions

The employment of UHP pre-treatment on recycled fibres allowed an improved removal of xylan in a xylanase-catalysed treatment. UHP pre-treatment promoted forced hydration of fibrils and the disaggregation of microfibrils, which ensued the opening of inter-fibrillar space for enzymatic attack. Due to improved accessibility enzymes were able to remove xylan more efficiently. This was demonstrated for both recycled and virgin fibres, for comparison, in terms of reducing sugars release and mass balance.

Moreover, although both fibres showed improved enzymatic accessibility the optimum pressure condition of UHP pre-treatment were different (400MPa for ***R*** and 500MPa for ***E***). It was suggested that due to the damaged cell wall of ***R***, this last required less severe hydrostatic pressure to disaggregate cellulose microfibrils than ***E*** (unbeaten virgin fibres with intact cell wall).

It was also demonstrated that the partial removal of xylan enabled the improvement of strength properties on both pulps, which were further improved when pulps were pre-treated by UHP treatment (more efficient enzymatic hydrolysis). Also, recycled fibres improved drainability suggest a better refinability, which is indicative of energy savings, as regards pulp refining in papermaking.

The results achieved also demonstrated the importance of pH conditions, close to neutral, during the enzymatic treatment. It was found that this was important to avoid the dissolution of fillers such as calcium carbonate, and thus avoid a decrease in brightness. Nevertheless, UHP pre-treatment revealed a favoured elimination of concomitant impurities, such as OBA, residual inks and auxiliary reagents in recycled pulp. However, under the treatment conditions (mild acidic pH without surfactants) the re-precipitation of impurities together with the loss of OBAs contributed for the decrease of recycled fibres brightness. Which was not the case of virgin pulp (increase of ca 0.5% ISO).

As main conclusion, it is suggested that the modification of hardwood-purified bleached recycled pulp by xylanase treatment was a very efficient tool for improving its papermaking properties. However, further studies are required on the development of papermaking properties during beating of the recycled pulp subjected to enzymatic treatment at variable xylanase loads, including the use of industrially produced enzymes and on the evaluation of economic feasibility of recycled pulp modification by UHP/enzymatic treatment.

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Chapter VI

Effect of ultra-high pressure on the impregnation of additives

- Dyes

Contents

6.1. Introduction

The competition in tissue paper market has stimulated the development of new products, more appealing to consumer, such as coloured papers. This approach of appealing to consumer's senses, by using a colour coding, or as a way of brand identification,[1,2] has led companies, such as Renova, to differentiate themselves from competition, for example in tissue paper market (e.g. Renova black toilet paper). The class of chemicals responsible for conferring colour to papers are dyes. This ancient class of additives are employed not only in paper industry, but also, and at a much larger scale, on textiles. [1–3] Dyes account for 5% of the specialty chemicals applied to paper. These colourants are added to paper stock at the preparation stage, to produce distinguished coloured papers.[1,2,4]

The selection of a suitable dye for paper coloration depends, for instance, on its end-use requirements, physical and chemical properties, and handling characteristics. Paper dyeing aims to produce paper with a desired colour or shade, although the dyeing process itself can be a rather complex one. [1,2] Several issues arise during pulp dyeing, some related with the interference of process variables, when dyes react differently with different furnishes, or due to the interaction of dyes with other additives (mostly by electrostatic interaction). [1,2,5] At the same time, some other parameters should be taken into consideration. For example, the fastness properties, which are of utter importance for high quality writing or tissue papers (e.g. paper in contact with food should exhibit insignificant or non-existent bleeding). Other properties include light fastness properties, toxicity and the environmental impact of the dyed product. [2]

In paper dyeing, direct dyes (anionic and cationic) as well as acidic and basic are the most widely used. Nevertheless, direct dyes occupy a central role in paper dying.[1,4,6,7] During the dying process dyes penetrate into fibres and interact with them. Considering the type of dyes, the established bonds may be intermolecular hydrogen interactions or electrostatic interactions. A dye molecule may also be precipitated on the fibre surface. In case of anionic direct dyes (used by Renova), those may interact with cellulosic fibres through Van der Wall forces and hydrogen bonds. Also, the aggregation ability with fibres may play a central role on the dye fixation. Due to the anionic nature of both direct anionic dyes and cellulose, in most cases a fixative agent (e.g. cationic fixatives) is used to enhance dye fixation (dye adsorption on fibres), in order to achieve an efficient dyeing process.

An efficient dye fixation is a rather relevant issue in coloured tissue paper production, since it is translated not only into a strongly coloured product (higher

retention/fixation), but also in the product fastness properties and effluents managements (coloured backwaters, increased chemical oxygen demand, etc.). [1,4,5]

Ultra-high pressure technology (UHP) emerges here as a potential prospective technology, to improve the dyeing of cellulosic fibres due to improved accessibility. The structural changes induced on fibres by UHP treatment, such as, disaggregation of microfibrils and forced hydration should increase accessible surface and diminish zeta potential of fibrils (two factors favouring dye fixation). The improved accessibility on cellulosic fibres has been demonstrated, in previous studies, towards chemicals and enzymes.[8–10] With this in mind, this study was focused on application of UHP treatment in the impregnation of fibres with dyes, commonly used by Renova for the tissue paper, and limiting the coloured paper production. The effect of dye fixation/retention, along with its fastness properties (namely bleedfastness) were evaluated.

6.2. Materials and Methods

Contrarily to the previous chapter, the raw material used in these studies was virgin hardwood pulp. This raw material was used as reference to avoid irregularities coming from the variability of recycled pulps lots. Such approach is justified from an academic point of view. Therefore, *Eucalyptus globulus* bleached *kraft* industrial pulp, ***E***, kindly supplied by Renova FPA, S.A. was used as reference raw material for the dyeing studies. The dyes and fixative agent tested, also supplied by Renova, were the following:

- Pergasol® Black GN-E (BASF, direct anionic dye, powder, azo dye)
- Pergasol® Red 7BE (BASF, direct anionic dye, powder, diazo dye)
- Pergasol® Violet BN-TKZ (BASF, direct anionic dye, liquid, diazo dye)
- Pergasol® 2G-Z (BASF, direct anionic dyes, liquid, azo dye)
- Cartasol Blue 3R-EU (Clariant, direct anionic dye, liquid, azo dye)
- Synthro®– Fix WF (Prox, cationic resin, 50% dry weight)

6.2.1. Preliminary tests with Pergasol Red 7BE-and Pergasol Black GNE

- Propylene Glycol (96%, Dowcal)
- Distilled water

Preliminary tests performed with Renova dyes (Pergasol Red 7BE and Pergasol Black GN-E), aimed to evaluate UHP abilities improving dye impregnation and fixation on pulp.

Since at this point the UHP equipment with higher capacity was not yet available, due to the limited capacity of the available one, and thus the insufficient amount of sample to produce standard handsheets, smaller handsheets were prepared under an adapted procedure. The small handsheets were prepared in laboratory through filtration, with a porous glass filter (no.3, Ø=60 mm). Firstly, 2%, 1% and 0.5% (w/v) of dye solutions (Pergasol Red 7BE and Pergasol Black GN-E) were prepared, together with a fixative (Synthro – Fix) solution of 0.05% (w/v). Pulp was weighted (1 g) and then dispersed in 100 mL of cationic resin solution. The dispersion was allowed to stir during 5 min for interaction with fibres and was then filtered. To the filtered pulp 44 mL of dye solution was added. Then, after the homogenization of the pulp dispersion, samples meant for UHP treatment were placed on plastic bags, vacuum sealed, and subjected to UHP treatment (400 MPa, 15 min), whereas non-treated samples were subjected to stirring for 15 min (reference).

The UHP treatment was performed using a High Pressure U33 device (Institute of High Pressure Physics, Poland), with a high pressure vessel of approximately 100 cm^3 capacity, filled with a pressure transmitting medium (propylene glycol:water, 1:1, v/v).

After impregnation, the coloured pulp suspensions were diluted up to 100 mL, with distilled water, homogenized and separated into equal dispersions of 20 mL. Each solution (20 mL x 0.2 g of pulp) was used to prepare small paper sheets by filtration through a glass porous filter. The wet paper sheets were collected and left drying on aluminium sheets overnight (~70 g/m^2). When dried, all paper sheets were evaluated on its smooth side with a CM-2300d spectrometer from Konica Minolta to access the colour intensity.

6.2.1.1. Optimization of UHP conditions (pressure and time)

These tests were carried out to perceive the UHP conditions (pressure and time) most advantageous for the pulp dyeing process. The used protocol was similar to that described in section **6.2.1**, although with small differences. The dye concentration was fixed at 1% (w/v). The tested dyes were Pergasol Black GN-E and Pergasol Red 7BE, at different UHP conditions 300 MPa (10, 20, 30 min), 400MPa (10, 20, 30 min) and 500 MPa (5, 10, 15 min). The UHP treatment was performed at the same equipment as described in section **6.2.1.** The procedure for paper sheets preparation was also the same as employed before and described in **6.2.1.** When dried, handsheets were evaluated on its smooth side with a CM-2300d spectrometer from Konica Minolta.

6.2.2. Determination of the optimum fixative load (OFL)

Due to the difficulties found for dyes fixation on pulp from relatively concentrated dye solutions, a new protocol was used, kindly suggested by Renova, to enable the determination of the amount of fixative required for an optimized dye fixation. The determination of the optimum fixative load (OFL), was determined considering an approximation of Renova norm PT.LAB.613, without UHP treatment, for the following dyes: Pergasol Black GN-E, Pergasol Red 7BE, Pergasol Violet BN-TKZ, Pergasol 2G-Z and Cartasol Blue 3R-EU.

Pulp suspensions of 16 g/L concentration were prepared by dispersing 0.4 g of pulp (dry weight) in 25 mL of distilled water. Each sample was then treated according to conditions presented in Table 6. 1. For these trials solutions of 2% (w/v) of dye and fixative were used. The required volume was calculated based on Table 6. 1 information.

Table 6. 1– Determination of the optimum fixative load (RENOVA PT.LAB.613).

Load	Fixative (%)($w_{fixative}/w_{pulp}$)	Stirring	Dye (%)(w_{dye}/w_{pulp})	Stirring	Fixative (%)($w_{fixative}/w_{pulp}$)	Stirring
1	0	1min	3	3min	0	1min
2	0.10				0.65	
3	0.20				1.50	
4	0.30				2.20	
5	0.40				2.60	
6	0.50				3.00	

Following the protocol described in Table 6. 1, each pulp suspension was diluted up to 100 mL, homogenised and divided into two equal dispersions of 50 mL each. These were further filtered on a glass porous filter (no.3, Ø=60 mm) and left drying on aluminium sheets overnight. When dried all paper sheets were evaluated on its smooth side with a CM-2300d spectrometer from Konica Minolta. The OFL values determined for each dye were compared with typical OFL values determined on Renova quality control, to verify any eventual differences in the results obtained.

6.2.2.1. Effect of UHP on fixative load variations

After determining the load of fixative required to achieve an optimum dye fixation, further tests after UHP treatment of pulp were conducted. These trials were carried out on a new 55L capacity equipment (high pressure apparatus, model 55 Hyperbaric). Since larger scale assays were possible, this enabled the production of standard handsheets on Renova facilities, in agreement with Renova norm PT.Lab.613.

Using the same dyes as in section **6.2.2.** (Pergasol Black GN-E, Pergasol Red 7BE, Pergasol Violet BN-TKZ, Pergasol 2G-Z, and Cartasol Blue 3R-EU)**,** and also considering each dye OFL (determined following section **6.2.2**), each sample was prepared individually in amounts enough to allow handsheet preparation on Renova's Rapid-Köthen sheet former (Karl Schröder KG).

In a typical experimental set pulp dispersions of 16 g/L concentration were prepared (2 g – 125 mL) with a dye load of 3% (w_{dye}/w_{pulp}). The dye and the fixative were applied following the order indicated in Table 6. 1, from 2% (w/v) dye and fixative solutions, prepared beforehand.

One set of samples was subjected to UHP (500 MPa, 10 min, in aqueous medium), while the other (reference) was just subjected to stirring. Then, both samples were used to prepare (~60 g/m^2). The effect of UHP on the dye fixation, by removing certain percentages of fixative, was also evaluated. These tests aimed to verify the UHP effect on a dye fixation, thus allowing the savings of fixative. Three types of samples were prepared, while reducing fixative by 5, 10 and 15% in relation to the expected amounts as indicated

in Table 6. 1. Each sample was also subjected to UHP (500 MPa, 10 min) or stirred only for comparative reasons (reference sample). The produced samples were used to prepare standard handsheets, and then were evaluated using a spectrometer from Konica Minolta, model CM-2300d.

6.2.3. Determination of fixative optimum load (OFL) after UHP treatment

The effect of UHP on the dye-fixative-substrate equilibrium was also studied (norm PT.Lab.613). Five sets of pulp suspensions of 16 g/L concentration (2 g x 125 mL each) were prepared and treated according with the steps described on Table 6. 1. Afterwards samples were vacuum sealed in HDPE flasks and subjected to UHP (500 MPa, 10 min – equipment model 55, Hyperbaric). The resultant samples were then used to produce standard handsheets on a Rapid-Köthen sheet former, for colour evaluation. The coloured handsheets were analysed on spectrometer from Konica Minolta, model CM-2300d.

6.2.4. Dye savings study

Pergasol Red 7BE was selected as a case study to evaluate the differences/similarities existing between different colour levels upon UHP treatment. The main purpose was to evaluate the ability of UHP to promote the dyeing of pulp fibres, thus saving the dye stock. Accordingly, 16 g/L pulp suspensions were prepared and dyed using Pergasol Red 7BE, with 3% (w/w) of dye load. Here the fixative and dye loads were those as in Table 6. 1 and Table 6. 2. The amount of fixative added was in agreement with the OFL UHP pre-determined as described in section **6.2.3.** (fixative concentration no. 6 for Pergasol Red 7BE). Afterwards, samples were subjected to UHP (500 MPa, 10 min) and used to produce handsheets. For comparative reasons, pulp samples dyed with 3 and 4% (w_{dye}/w_{pulp}) dye concentration were also prepared. In these cases, the fixative amount added was in agreement with the OFL determined without UHP (fixative concentration no. 4 for Pergasol Red 7BE).

Table 6. 2 – Dye charges versus fixative loadings.

Dye load (%) (w_{dye}/w_{pulp})	Fixative (%) ($w_{fixative}/w_{pulp}$)											
	1		2		3		4		5		6	
	initial	final	initial	final	initial	final	initial	final	initial	final	initial	final
3.00	*0.000*	*0.000*	*0.100*	*0.650*	*0.200*	*1.500*	*0.300*	*2.200*	*0.400*	*2.600*	*0.500*	*3.000*
4.00	0.000	0.000	0.100	0.900	0.200	1.800	0.300	2.700	0.400	3.600	0.500	4.500

6.2.5. Coloured papers evaluation

6.2.5.1. Colour and spectral data

Colour and spectral data, such as L*a*b, ΔE and $K/S(\lambda_{max})$ were obtained by analysis of coloured paper sheets. These parameters were also acquired for bleedfastness tests on a spectrometer from Konica Minolta, model CM-2300d. Each measurement was the result of 4 measurements in different sites of each sample. The evaluation of the magnitude of colour variation was performed considering Table 2.6 from ***Chapter 2***.

6.2.5.2. Colour fastness

- Acetic acid (99%, VWR)
- Saliva simulant (Renova)
- Olive oil (Renova)
- Distilled water

Colour fastness tests were performed in Renova's Laboratories, in agreement with a Renova's norm PT.LAB.327, which is based on norms EN646:2006 ("Paper and board intended to come into contact with foodstuff – Determination of colour fastness of dyed paper and board") and ISO 105-A03:1993 ("Textiles – Tests for colour fastness – Part A03 Grey scale for assessing staining").

For these tests, test pieces of coloured papers (dimensions 50 mm x 20 mm) were prepared and subjected to different media, namely distilled water, acetic acid (3% (w/v)), saliva simulant and olive oil. Firstly, two sheets of unstained glass fibre paper (dimension 60 mmx45 mm) were immersed in a test fluid and removed after saturation. The excess fluid was removed. Then, one sheet of the saturated unstained glass fibre paper (smooth side upwards) was placed on a glass plate (dimensions 60 mm x90 mm). Immediately after, a test paper piece was placed on the unstained glass fibre paper, and was then covered by the second saturated unstained glass fibre paper (smooth side in contact with the test piece). Then, this last was further covered by a second glass plate. Finally, a mass of 1 Kg was placed on top of the abovementioned assembly, and kept protected from direct light penetration for 10 min. Afterwards, the glass fibre papers were removed and when dried these last were analysed using a spectrometer (CM-2300d from Konica Minolta). The acquired data was analysed in terms of ΔE (determined based on the colour coordinated of the stained glass papers and an unstained one (reference)). The acquired values were analyses for colour fastness in agreement to Table 6. 3.

Table 6. 3 – Degree of fastness relationships with ΔE.

Degree of fastness	ΔE	Tolerance
5	0	±0.2
4	4.3	±0.3
3	8.5	±0.5
2	16.9	±1.0
1	34.1	±2.0

6.2.6. Zeta potential

Zeta potential analysis was performed on a *Malvern Zeta Sizer Nano Series*, apparatus using disposable plastic cells on pulp diluted dispersions and dye diluted solutions. Complementarily each solution pH was also measured using a pH Meter, model HI2020 - edge® multiparameter, from Hanna Instruments.

6.3. Results and Discussion

As previously depicted the impregnation studies with dyes were performed using solely using virgin hardwood fibres as reference raw material to avoid irregularities coming from different lots of recycled pulps.

6.3.1. Preliminary tests

Preliminary tests with two dyes supplied by Renova were performed as described in section **6.2.1.** These tests aimed to study differences that could emerge by employing UHP treatment on fibres dyeing process. The dyes selected were the two of the most problematic for Renova, Pergasol Red 7BE and Pergasol Black GN-E. The conditions applied were standard UHP conditions, used in previous assays (400 MPa, 15 min). For each dye, three sets of pulp samples (treated in advance with fixative agent) were impregnated with 2, 1 and 0.5% ($w_{dye}/v_{solution}$) dye solutions. Since at this stage the pilot UHP equipment of high capacity (55 L) was not yet available, and due to the low capacity (100 mL) of the existing one, the produced paper sheets were prepared by filtration of a diluted and homogenous dispersion of each sample, yielding handsheets with approximately 70 g/m^2.

The colorimetric and spectral data from each sample, namely L*a*b, and $K/S(\lambda_{max})$ (measurement of intensity/concentration), respectively, were collected and are presented in Table 6. 4 and 6. 5. For simplicity, in both cases, samples treated with UHP were labelled "*X% with UHP"*, while untreated samples were labelled "*X% without UHP"*, where *X%* is the concentration of the dye solution used in the dyeing process.

In Table 6. 4 it possible to observe the results achieved for samples impregnated with Pergasol Red 7BE. In this case, samples revealed higher *K/S* after UHP treatment, than in the assay without UHP, which imply an improved dye penetration and fixation on cellulosic fibres. From the L*a*b coordinates the differences in colour between untreated and UHP treated samples (ΔE*)* were determined. All UHP treated samples exhibited clear colour differences, being the most significant achieved for samples dyed with the lowest dye load (with 0.5% (w/v) dye solution). The set of samples impregnated with 2% (w/v) exhibited a ΔE between 1 and 2, meaning that the colour difference was small, only perceptible to experienced observers (Table 2. 6, ***Chapter 2***).[11] . Additionally, both samples sets impregnated with 0.5% (w/v) and 1% (w/v), exhibited a ΔE between 2 and 3.5, which imply a perceivable colour difference between non-treated and UHP treated samples.

Both colorimetric and spectral data suggest higher colour intensities in UHP treated samples, which imply a higher dye fixation. As demonstrated in previous chapters and in the literature,[8–10] UHP treatment promotes forced hydration of fibrils, yielding their disaggregation and improved accessibility. In this case, the use of UHP treatment, for dye impregnation, has enabled a more efficient penetration of dye molecules, with fixative agent molecules, into the fibrillary structure, than without the application of UHP. As result an increased amount of dye molecules were retained, yielding higher colour intensity.

Table 6. 4 – Colorimetric and spectral data collected for samples dyed with Pergasol Red 7BE.

Dye	Sample	$K/S(\lambda_{max})$	L*	a*	b*	Colour	ΔE*
Pergasol Red 7BE	*0.5% without UHP	4.17±0.18	51.77±0.30	48.42±0.23	-5.47±0.12		3.05
	0.5% with UHP	5.24±0.20	49.19±0.27	49.98±0.28	-4.74±0.10		
	*1% without UHP	7.94±0.30	44.67±0.31	52.19±0.18	-1.68±0.15		2.46
	1% with UHP	9.46±0.31	42.61±0.25	52.58±0.19	-0.4±0.20		
	*2% without UHP	11.89±0.20	39.43±0.31	51.8±0.18	2.3±0.15		1.82
	2% with UHP	13.53±0.23	38.02±0.28	51.91±0.15	3.44±0.18		

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

In the case of Pergasol Black GN-E (Table 6. 5) a slightly different behaviour was registered. Upon UHP, samples impregnated with 0.5% (w/v) dye solution displayed a slightly lower *K/S*, while, on the other hand, samples impregnated with 1 and 2% (w/v) dye solutions displayed higher *K/S* after the UHP treatment. These differences, relatively to Pergasol Red 7BE, suggest that the differences existing between both dye molecules structure affect the interaction between dye and cellulose. From the colour coordinates the ΔE values were also determined. The samples treated with the lowest dye concentration exhibited a value of 3.42, which is in the range of perceivable colour difference, towards a less intense colouration. On the other hand, other samples, treated by UHP, registered some improvements in dyeing. In the case of 1 and 2% (w/v) load of the dye a ΔE of 1.44 and 0.85 (only perceivable to experienced observers), were registered, respectively.

Although, in some cases, UHP treatment revealed enhanced impregnation, as expected, the variation found suggests changes on the fixation process related, possibly, with the differences existing between the molecular structures of the two dyes.

Table 6. 5 - Colorimetric and spectral data collected for samples dyed with Pergasol Black GN-E.

Dye	Sample	$K/S(\lambda_{max})$	L*	a*	b*	Colour	ΔE*
Pergasol Black GN-E	*0.5% without UHP	9.03±0.23	31.18±0.21	-2.52±0.15	-4.07±0.17		3.42
	0.5% with UHP	8.59±0.20	34.4±0.23	-3.58±0.20	-4.5±0.16		
	*1% without UHP	11.50±0.10	27.47±0.30	-2.46±0.18	-3.58±0.30		1.44
	1% with UHP	11.59±0.11	28.8±0.29	-2.91±0.17	-3.89±0.29		
	*2% without UHP	13.28±0.41	23.87±0.45	-1.38±0.15	-2.37±0.32		0.85
	2% with UHP	13.59±0.42	24.46±0.41	-1.82±0.13	-2.80±0.35		

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

6.3.1.1. Effect of UHP conditions

The most advantageous UHP conditions (pressure and time) for the impregnation process with dyes were also studied. Dyeing tests were performed as described before (section **6.3.1.**), with Pergasol Red 7BE and Pergasol Black GN-E, for fixed dye load (pulps were impregnated with a 1% (w/v) dye solution) at different time (10-30 min) and pressure conditions (300-500 MPa).

The colorimetric and spectral data acquired from each sample are presented in Table 6. 6 for samples dyed with Pergasol Red 7BE, and in Table 6. 7 for samples dyed with Pergasol Black GN-E. As concerns Pergasol Red 7BE, (Table 6. 6) it is possible to observe that an increase in pressure and time of UHP treatment led to an increase of *K/S* in treated pulps. Although, considering the acquired data, the conditions conveying higher *K/S* were 300 MPa/20 min, followed by 400 MPa/30 min and 500 MPa/10 min.

Similarly, to Pergasol Red 7BE, the results for Pergasol Black GN-E (Table 6. 7) also demonstrated that longer pressurization times and higher pressure conditions applied, resulted in higher *K/S* values. The best results, in terms of *K/S*, were achieved for 500 MPa and 10 min of pressurization.

However, considering time as a relevant factor in pulp processing, and the data obtained from the studies of both dyes, 500 MPa and 10 min were selected as the optimum conditions, due to the highest *K/S* values achieved with both dyes (measurement of colour density on fibres). The values of (*K/S*) are also frequently used at Renova Laboratories as criteria for the selection of optimum conditions.

Table 6. 6 – Colorimetric and spectral data acquired for Pergasol Red 7BE samples, dyed at different conditions.

Dye	Pressure conditions	*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE*
Pergasol Red 7BE (1%(w/v))	Without UHP	9.87±0.11	44.67±0.20	52.19±0.12	-1.68±0.11		-
	300MPa,10min	10.68±0.05	42.55±0.09	53.18±0.13	-0.14±0.15		2.80
	300MPa, 20min	11.13±0.30	41.4±0.37	52.94±0.12	0.79±0.35		4.67
	300MPa, 30min	9.99±0.23	40.45±0.25	52.29±0.23	1.57±0.14		5.33
	400MPa, 10min	10.11±0.12	42.27±0.34	52.88±0.19	0.17±0.30		3.11
	400MPa, 20min	9.93±0.33	42.2±0.34	53.08±0.18	0.29±0.19		3.28
	400MPa, 30min	10.86±0.17	42.66±0.21	53.4±0.18	-0.18±0.12		2.78
	500MPa, 5min	10.18±0.15	41.39±0.30	53.14±0.29	0.98±0.30		4.33
	500MPa, 10min	10.73±0.59	42.09±0.76	53.00±0.25	0.39±0.83		3.41
	500MPa, 15min	9.87±0.45	41.29±0.46	52.74±0.20	1.00±0.29		4.35

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

Table 6. 7 - Colorimetric and spectral data acquired for Pergasol Black GN-E samples, dyed at different conditions.

Dye	Pressure conditions	*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE
Pergasol Black GN-E	*Without UHP	11,44±0.12	27.47±0.30	-2.46±0.15	-3.58±0.13		-
	300MPa,10min	10,11±0.36	28.43±0.54	-2.15±0.14	-4.72±0.17		1.52
	300MPa, 20min	10,43±0.09	28.07±0.21	-2.15±0.10	-4.82±0.17		1.41
	300MPa, 30min	10,37±0.21	28.01±0.48	-2.08±0.22	-4.51±0.31		1.14
	400MPa, 10min	10,78±0.13	27.35±0.45	-2.01±0.39	-4.23±0.55		0.80
	400MPa, 20min	10,81±0.19	27.06±0.74	-1.86±0.48	-4.04±0.66		0.86
	400MPa, 30min	13,65±0.59	24.26±0.26	-1.72±0.43	-2.90±0.61		3.36
	500MPa, 5min	13,02±0.61	23.40±0.25	-0.80±0.44	-1.62±0.60		4.81
	500MPa, 10min	14,68±0.58	22.89±0.18	-1.47±0.47	-2.39±0.73		4.83
	500MPa, 15min	14,48±0.46	23.12±0.73	-1.56±0.66	-2.42±1.05		4.59

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

The improved results on dyeing at long pressurization times and high pressures are in agreement with the severity of the UHP treatment applied. These UHP conditions provide the highest accessibility of fibres, favouring the best conditions for the adsorption of dyes.

Nevertheless, results of section **6.3.1**., revealed some discrepancy in results. At constant fixative load, by varying the dye concentration, the colour intensity of handsheets should increase with the increase of dye concentration in solution. However, it was not always the case. In these preliminary studies, in order to reveal the UHP effects, a minimal amount of fixative agent was used. However, it seems that the fixative agent plays a rather relevant role as intermediate of the dye fixation process and requires specific adjustments for each dye.

Despite during UHP treatment the accessibility of fibres increase and its zeta potential decreases, the still high negative charge of fibres requires some additional amounts of fixative agent to improve dyes adsorption. This is confirmed by zeta potential measurements of pulp and of a dye solution (Pergasol Black GN-E) (Table 6. 8).

Bearing in mind the aforementioned result, the determination of the fixative optimum load (OFL), was required.

Table 6. 8 – Zeta potential measurements of a Pergasol Black GN-E solution and of pulp treated with and without UHP (***EHP*** and ***E***, respectively).

Sample	Zeta Potential (mV)	pH
E	-15.4±3.5	5.9
E HP	-9.9±5.6	5.7
Pergasol Black GNE solution	-20.7±1.62	5.7

6.3.2. Optimization of fixative loads

6.3.2.1. Optimum fixative load (OFL) without UHP treatment

The importance of fixative agent concentrations on the dyeing process of bleached kraft hardwood pulp was studied. Hence assays were performed to determine the load of fixative agent required to ensure optimum dyeing, under conventional impregnation (without UHP treatment). In these studies, Renova norm PT.LAB.613 was followed, as depicted in section **6.2.2**. Besides, the determination of the optimum fixative load (OFL) was performed with other dyes. The other dyes include Cartasol Blue 3R-EU, Pergasol Violet BN-TKZ and Pergasol Red 2G-Z. The aim of this study was to relate the fibre dyeing with the molecular structure of dye molecules and different dyes furnishes (powder or liquid).

In those tests six different loads of fixative agent were tested, as displayed in Table 6. 9. In each loading the fixative must be applied in two stages, one at the beginning, before adding the dye, and then, the other at the end, after the addition and dispersion of the dye. The initial step of fixative agent addition is related with the necessity of increasing zeta potential of cellulosic fibres, to assist their interaction with dyes due to the existing electrostatic repulsion between them. Then, dye molecules are added and should interact more easily with cellulosic fibres due to the presence of a cationic intermediate (fixative agent). The final addition of fixative acts as a way to precipitate the remaining dye on fibres surface. This may occur by the formation of insoluble dye-fixative particles that precipitates on the fibres surface.

As concerns the determination of the optimum fixative loads, the procedure was performed at fixed dye load (3% (w_{dye}/w_{pulp})), with different fixative loads (Table 6. 9).

Table 6. 9 – Different fixative loads for 3% (w_{dye}/w_{pulp}) of dye concentration.

Dye % (w_{dye}/w_{pulp})	Fixative % ($w_{fixative}/w_{pulp}$)											
	1		**2**		**3**		**4**		**5**		**6**	
3.00	Start	End	Start	End	Start	End	Start	End	Start	End	Start	End
	0.000	0.000	0.100	0.650	0.200	1.500	0.300	2.200	0.400	2.600	0.500	3.000

To perceive which load of fixing agent would be more advantageous, according to Renova norms (Renova PT.LAB 613), *K/S* was used as criteria. The results upon each dye OFL are given by Table 6. 10.

Table 6. 10 – Determination of the OFL, without UHP, on dyes supplied by Renova.

Dye	Fixative loads	*K/S* (λ_{max})	OFL without UHP	Dye	Fixative loads	*K/S* (λ_{max})	OFL without UHP
Pergasol Red 7BE	1	0.23±0.003	**4**	**Pergasol Black GN-E**	1	0.1-±0.01	**3**
	2	0.59±0.03			2	1.02±0.02	
	3	2.61±0.22			3	4.76±0.17	
	4	3.26±0.007			4	3.63±0.02	
	5	2.68±0.23			5	2.14±0.21	
	6	2.31±0.04			6	2.19±0.14	
Pergasol Violet BN-TKZ	1	0.1±0.005	**2**	**Cartasol Azul 3R-EU**	1	0.085±0.02	**4**
	2	3.05±0.26			2	1.188±0.05	
	3	1.81±0.11			3	1.15±0.01	
	4	2.03±0.17			4	1.193±0.04	
	5	1.81±0.09			5	0.92±0.04	
	6	1.77±0.16			6	0.85±0.02	
Pergasol Red 2G-Z	1	0.07±0.005	**2**				
	2	2.19±0.008					
	3	1.38±0.12					
	4	1.32±0.021					
	5	1.22±0.011					
	6	1.15±0.03					

The values of *K/S* of dyed paper sheets, with each dye, suggest an increasing of dye fixation with fixative agent content that reaches a maximum followed by a decrease. These features reflect possibly the necessity of fixative molecules to act as an intermediate for the dye fixation process. After reaching the maximum (*K/S*), the existence of excess of fixative load in solution may possibly contribute for its dispersion in solution. By recharging of the

double layer in fibres and micelles of dyes, less amount of dye interacts and is retained by fibres. Apparently this favoured the decrease of *K/S* values in hand sheets.

Considering the *K/S* values in Table 6. 10, it was possible to conclude that the OFL (considering the fixative additions in Table 6. 9) for Pergasol Red 7BE was no. 4, for Pergasol Black GN-E was no. 3, for Pergasol Violet BN-TKZ was no. 2, for Cartasol Blue 3R-EU was no. 4 and for Pergasol Red 2G-Z was no. 2.

6.3.2.2. UHP effect on the impregnation of pulps with different dyes

After determining the OFL of each dye, a set of new tests was performed, but now resorting to UHP treatment. The UHP conditions were selected considering the results obtained in section **6.3.1.1** and were as follows: 500 MPa pressure and 10 min. Additionally, the decrease of fixative agent load by 5, 10 and 15% of fixing agent load, upon UHP, was also tested. These changes on fixative loads aimed to evaluate when UHP would convey similar or better results, while allowing fixative savings.

It is noteworthy that, at this point, a new UHP equipment, with higher capacity (55 L), was available, which allowed the preparation of all samples in sufficient amount to produce standard handsheets. All samples were evaluated considering its *K/S* (λ_{max}) value and colour space data. These studies were further completed with colour fastness tests, following the procedure presented in section **6.2.5.2**. These tests were performed to evaluate the colour fastness of each sample, since in case of coloured tissue paper it is required insignificant or zero dye bleeding. For simplicity samples were designated as follows:

3% without UHP – pulp dyed with a dye load of 3% (w_{dye}/w_{pulp}), not subjected to UHP;

3% with UHP – pulp dyed with a dye load of 3 %(w_{dye}/w_{pulp}), subjected to UHP;

3% with UHP | -5% fixatives – pulp dyed with a dye load of 3% (w_{dye}/w_{pulp}), subjected to UHP, whose OFL was reduced by 5%;

3% with UHP | -10% fixatives – pulp dyed with a dye load of 3% (w_{dye}/w_{pulp}), subjected to UHP, whose OFL was reduced by 10%;

3% with UHP | -15% fixatives – pulp dyed with a dye load of 3% (w_{dye}/w_{pulp}), subjected to UHP, whose OFL was reduced by 15%.

i) Pergasol Red 7BE

The data for samples dyed with Pergasol Red 7BE is presented in Table 6. 11. The achieved results allow to confirm the ability of UHP to enhance dye fixation on fibres. By comparing samples impregnated in 3% (w/w) dye load, with and without UHP, it was

possible to observe a much higher *K/S* in the case of UHP treated sample. Also, the high ΔE (7.05) indicated a substantial colour gain by fibres. These results evidenced the abilities of UHP to improve the fibres accessibility and the capacity of dyeing. Moreover, even with removal of 5, 10 and even 15% fixative, it was still possible to maintain the relatively higher dye fixation on fibres, as confirmed by the high *K/S* values and the colour differences expressed by ΔE.

Each sample bleedfastness was also analysed considering four diffusion media (water, acetic acid, synthetic saliva and olive oil). The results are represented in Table D.1 in the Appendices, and did not exhibited variations. This points no effects on the dye fixation on fibres caused by UHP treatment and the amount of fixative used.

Table 6. 11 - Colorimetric and spectral data collected for samples dyed with Pergasol Red 7BE.

Pergasol Red 7BE						
Sample		*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE*
*3% without UHP		2.12±0.04	57.03±0.22	35.36±0.39	-4.85±0.11		-
3% with UHP		3.20±0.18	52.15±0.51	40.06±0.59	-2.89±0.14		7.05
	-5% Fixatives	3.03±0.07	52.55±0.29	38.91±0.23	-3.13±0.12		5.97
3% with UHP	-10% Fixatives	3.11±0.06	52.41±0.16	39.94±0.58	-2.7±0.20		6.85
	-15% Fixatives	2.51±0.02	55.21±0.05	38.39±0.49	-4.05±0.23		3.62

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

ii) Pergasol Black GN-E

As concerns Pergasol Black GN-E (Table 6. 12), here the results diverged from those achieved with Pergasol Red 7BE. After UHP treatment the *K/S* of samples decreased in relation to non-treated samples, yielding a significant colour difference (lighter shade). Moreover, when removing fixative, the results either maintained or decreased even more. These features indicate that the fixative load, determined without UHP, is not enough to sustain the dye impregnation/fixation with UHP. Possibly, due to the dye molecules nature, a preferential impregnation with fixative is occurring. Thus, remaining fixatives molecules may not be enough to intermediate the process of approximation between cellulose and anionic dye. In this case UHP may have caused disturbances on the equilibrium between dye-fixative-cellulose and hence changing the required amount of fixative, for dye fixation, with UHP. It is noteworthy that dye molecules structures are not known. Additionally, it is also unknown whether dyes are made solely by one type of molecule of by a mixture of dye molecules.

Table 6. 12 – Colorimetric and spectral data collected for samples dyed with Pergasol Black GN-E.

Pergasol Black GN-E							
Sample		*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE*
*3% without UHP		4.1±0.07	39.01±0.3	-0.54±0.08	-2.3±0.03		-
3% with UHP		3.0±0.05	44.32±0.27	-0.94±0.006	-2.91±0.02		5.36
	-5% Fixatives	3.1±0.02	43.72±0.07	-0.86±0.04	-2.92±0.03		4.76
3% with UHP	-10% Fixatives	3.0±0.03	44.24±0.18	-0.94±0.02	-2.95±0.03		5.29
	-15% Fixatives	2.1±0.07	49.92±0.58	-1.12±0.03	-2.94±0.07		10.94

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

Similarly to previously tested dye, bleedfastness tests were carried out (Table D. 2 from the Appendices), although no significant changes were registered. These results suggest that the dye fixation on fibres was not affected by UHP treatment and the amount of fixative used.

iii) Cartasol Blue 3R-EU

Cartasol Blue, similarly to the above dyes, is also a direct anionic dye, although supplied in the liquid form. The results on pulp dyeing with this dye are presented in Table 6. 13.

Table 6. 13 - Colorimetric and spectral data collected for samples dyed with Cartasol Blue 3R-EU.

Cartasol Blue 3R-EU							
Sample		*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE*
3% without UHP		1.67±0.02	56.08±0.14	9.33±0.04	-23.25±0.11		-
3% with UHP		1.74±0.05	55.41±0.05	9.74±0.07	-23.64±0.04		0.88
	-5% Fixatives	1.77±0.009	55.15±0.06	9.82±0.09	-23.69±0.07		1.14
3% with UHP	-10% Fixatives	1.66±0.002	55.91±0.02	10.30±0.02	-22.84±0.04		1.07
	-15% Fixatives	1.84±0.02	54.51±0.14	10.79±0.05	-23.70±0.06		2.19

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

The results obtained with Cartasol Blue 3R-EU revealed, similarly to Pergasol Red 7BE, an improvement of dye adsorption on fibres, upon UHP treatment. This fact was confirmed by the increased *K/S* and the ΔE of 0.88. Also, upon diminishing of fixative, *K/S* did vary significantly, being even registered higher values of *K/S*, with 15% decrease of fixative agent, than with full charge. In terms of colour difference, the ΔE was of 2.19, which is in the range of perceivable colour difference by unexperienced observers. These results corroborate the aforementioned hypothesis that UHP should affect the existing equilibrium between dye, fixative and cellulose, which imply a shift on the OFL. Colour

fastness results (Table D.3 on the Appendices) also demonstrated no significant variations between assays. Therefore, it is possible to suggest that dye fixation on fibres was not affected by UHP treatment and by the amount of fixative used.

iv) Pergasol Red 2G-Z

The results acquired with Pergasol Red 2G-Z samples are depicted in Table 6. 14. In opposite to previous results, *K/S* decreased from 2.14 to 1.83, after impregnation with UHP treatment, with a perceivable colour difference, when considering ΔE (lighter shade). Moreover, the decrease in *K/S* became even more significant upon fixative removal. It is possible that the balance existing between the three intervening parts (dye, fixative and cellulose) may be shifted due to UHP treatment. Thus, it is possible, once more, that the different fixative load is required. It is also important to recall that low amounts of fixative decrease the dye fixation, and the excess of fixative could originate dye dispersion in solution, and hence evading its fixation onto fibres.

Table 6. 14 - Colorimetric and spectral data collected for samples dyed with Pergasol Red 2G-Z samples.

Pergasol Red 2G-Z						
Sample		*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE*
*3% without UHP		2.14±0.03	61.9±0.06	42.01±0.39	16.06±0.28		-
3% with UHP		1.83±0.03	63.43±0.16	40.16±0.39	14.38±0.17		2.93
3% with UHP	-5% Fixatives	1.72±0.01	63.84±0.09	39.33±0.50	13.89±0.28		3.96
	-10% Fixatives	1.48±0.07	65.20±0.44	37.71±0.50	12.75±0.28		6.35
	-15% Fixatives	1.36±0.009	66.01±0.06	36.86±0.14	11.89±0.13		7.78

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

Similarly to before, bleedfastness was also accessed for all samples and its results are represented on Table D.4 on the Appendices. Alike the previous cases, no changes on the fibres bleedfastness were registered.

v) Pergasol Violet BN-TKZ

Finally, pulp dyeing was performed by applying Pergasol Violet BN-TKZ (Table 6. 15). Samples impregnated with 3% (w/w) dye, upon UHP treatment revealed a decrease of *K/S*, which according to colour space coordinates registered a minimal colour difference, ΔE. Although the reducing of 5% fixative load, upon UHP treatment, yielded an increase of *K/S*, the diminishing of *K/S* was observed when the fixative reduction was 10 or 15%. These *K/S* values were accompanied by ΔE.

As concerns bleedfastness, no changes were registered in al assays. (Table C.5 from the Appendices)

Table 6. 15 - Colorimetric and spectral data collected for samples dyed with Pergasol Violet BN-TKZ.

Pergasol Violet BN-TKZ							
Sample		*K/S* (λ_{max})	L*	a*	b*	Colour	ΔE
3% without UHP		2.37±0.03	49.98±0.17	16.49±0.09	-18.02±0.03		-
3% with UHP		2.22±0.03	50.91±0.22	15.97±0.13	-19.03±0.11		1.47
3% with UHP	-5% Fixatives	2.60±0.02	48.72±0.13	17.01±0.26	-19.66±0.07		2.13
	-10% Fixatives	2.10±0.04	51.73±0.26	15.44±0.24	-18.33±0.01		2.06
	-15% Fixatives	2.31±0.06	50.30±0.41	15.54±0.15	-19.10±0.11		1.47

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

6.3.2.3. Optimum fixative load (OFL) after UHP treatment

Due to the divergence in previously obtained results, it was necessary to determine the optimum fixative load (OFL) after the UHP treatment, similarly as it was done for the dyeing without UHP treatment (section **6.3.2.1.**). The UHP conditions were as follows: pressure - 500MPa, duration – 10min.

i) Pergasol Red 7BE

Although previous results demonstrated the improvements of this dye adsorption in fibres (Table 6. 11), OFL was determined again, now after UHP treatment. The results obtained are summarised in Table 6.16 and 6.17. In Table 6. 16 it is possible to observe the *K/S* and colour space data for each fixative load (no. 1, 2, 3, 4, 5 and 6, as indicated in Table 6. 9). Here the highest *K/S* was used as criteria in the process of selection of the OFL, which was 6.

Table 6. 16 - Colorimetric and spectral data obtained with Pergasol Red 7BE, for different fixative loads for UHP processed pulp.

Pergasol Red 7BE							
Dye load	Fixative loads	*K/S* (λ_{max})	L*	a*	b*	Colour	OFL with UHP
3% (w_{dye}/w_{pulp})	1	0.67±0.02	75.20±0.21	31.68±0.02	-6.13±0.05		6
	2	0.94±0.01	70.74±0.07	34.72±0.15	-6.55±0.05		
	3	2.30±0.02	57.68±0.05	38.32±0.19	-4.88±0.04		
	4	2.73±0.03	55.04±0.11	39.10±0.09	-4.03±0.08		
	5	2.82±0.03	54.58±0.13	39.07±0.27	-3.84±0.10		
	6	3.15±0.02	53.58±0.07	39.91±0.18	-3.60±0.05		

*ΔE determined for each UHP processed sample in comparison to sample dyed without UHP.

Relatively to the OFL without UHP treatment (load 4 in Table 6. 17), this shift towards a higher load of fixative agent (load no.6 in Table 6. 17), suggests an increased demand on fixative, possibly due to a preferential insertion of the cationic resin (fixative) in fibres. Together with improved dye diffusion into fibres, due to UHP treatment, this last factor could have contributed for the efficient fixation of dye molecules on fibres. Such enhanced dyeing efficiency, with increased OFL, was evidenced both by *K/S* and ΔE values. It is worth to note that an enhanced dyeing efficiency may lead to the diminishing of organic charge in the mill effluent and hence creating fewer problems in residual waters treatment. It is also reasonable to propose that these improvements could lead to deep colour shades without resorting to higher dye loading. This was a topic of further studies.

Table 6. 17 – Comparison between colorimetric and spectral data obtained with and without UHP processing of pulp dyed with Pergasol Red 7BE.

	Pergasol Red 7BE						
OFL	*K/S* (λ_{max})	L*	a*	b*	Colour	Δ(*K/S*$_{max}$)%	ΔE
OFL without UHP 4	2.12±0.04	57.03±0.22	35.36±0.39	-4.85±0.11			
						+48.6	5.84
OFL with UHP 6	3.15±0.02	53.58±0.07	39.91±0.18	-3.60±0.05			

The bleedfastness (Table D.1, Appendices) was also accessed and the results revealed no significant variations among samples (bleedfastness degrees between 4 and 5) of dyed hand sheets, produced from UHP treated and untreated pulps. Small variations were only found between 4 and 5 bleedfastness degree on samples from OFL after UHP treatment, possibly due to the variation of fixative amount.

ii) Pergasol Black GN-E

Considering the variations found on previous results, Pergasol Black GN-E was also tested for a OFL with UHP. The results attained are presented in Table 6. 18. There, it is possible to observe the colour space and spectral data for each fixative load (no. 1, 2, 3, 4, 5 and 6, as depicted in Table 6. 1) upon UHP (500 MPa, 15 min). *K/S* was used as the criteria, being selected, as the OFL with UHP the sample with the highest *K/S* value. The OFL with UHP, according to the acquired data, was no. 5, which implies a shift towards higher fixative loadings, when compared with the OFL without UHP (load no. 3). However, a higher coloration of pulp was attained with the OFL after UHP, relatively to OFL without UHP treatment.

By comparing both OFLs, determined with and without UHP (Table 6. 19), similarly to Pergasol Red 7BE case, the observed change towards higher fixative loadings suggests

shifts on equilibrium between dye-fixative and cellulose, which could be related with an increased adsorption of fixative on fibres. Apparently, this increased load was not enough to cause the dye dispersion in solution, but induced a higher improved dye fixation on fibres. Hence, OFL after UHP treatment exhibited an increased *K/S*, with a ΔE superior to 5, i.e. a clearly distinguished colour gain.

Table 6. 18 - Colorimetric and spectral data obtained for Pergasol Black GN-E coloured samples, for different fixative loads for UHP processed pulp.

Pergasol Black GN-E							
Dye load	Fixative loads	*K/S* (λ_{max})	L*	a*	b*	Colour	OFL UHP
3% (w_{dye}/w_{pulp})	1	0.46±0.007	75.90±0.15	-4.74±0.02	-4.44±0.05		5
	2	0.99±0.02	63.51±0.28	-3.15±0.03	-4.52±0.05		
	3	3.95±0.07	39.25±0.33	-0.35±0.03	-2.28±0.09		
	4	4.50±0.03	37.18±0.12	-0.28±0.02	-1.91±0.006		
	5	5.20±0.05	34.85±0.18	-0.18±0.05	-1.45±0.05		
	6	4.92±0.08	35.85±0.29	-0.37±0.03	-1.58±0.10		

Table 6. 19 - Comparison between colorimetric and spectral data from Pergasol Black GN-E samples, namely for OFL without UHP and with UHP.

Pergasol Black GN-E							
OFL	*K/S* (λ_{max})	L*	a*	b*	Colour	Δ(K/S_{max})%	ΔE
OFL without UHP 3	4.1±0.07	39.01±0.3	0.54±0.08	2.30±0.025		+26.8	5.64
OFL with UHP 5	5.20±0.05	34.85±0.18	-0.18±0.05	-1.45±0.05			

The bleedfastness (Table D.2, Appendices) alike before, was analysed and its results revealed no significant changes in terms of bleedfastness degrees (between 4 and 5). The most significant variations (which were still small) were found on the samples for the determination of OFL with UHP, possibly due to fixative variation.

iii) Cartasol Blue 3R-EU

Cartasol Blue 3R-EU was also examined for OFL after UHP treatment. The results obtained with different fixative loads are displayed in Table 6. 20. In contrast to the two previous dyes (Pergasol Black GN-E and Pergasol Red 7BE), it was found a shift towards lower fixative loading (from no.4 to 2) of OFL after UHP, relatively to OFL without UHP treatment. Besides, samples impregnated after UHP still exhibited higher *K/S* than without UHP treatments (Table 6. 21).

The OFL after UHP treatment was determined based on the fixative load rendering the highest *K/S*, which was load no. 2. The decrease found on the required load of fixative,

to achieve the optimum dye fixation could be related, not directly to a preferential adsorption of fixative on fibres, but with a decreased repulsion between this dye molecules and cellulose. It is known that different dye molecules, although anionic, may interact differently (more or less strongly attracted to cellulose) due to its structural peculiarities. The planar geometry of most direct anionic dyes, favours significantly the interactions with cellulose. Nevertheless, although the dye molecule charge (located in some part of the molecule) convey some repulsion towards cellulose, other functional groups or even its carbon backbone, may interact with cellulose through other mechanisms. Thus it is possible that Cartasol Blue 3R-EU, upon UHP, was adsorbed more efficiently on fibres, possibly, due to its improved affinity towards cellulose (decreased repulsion in relation to other dyes). Hence, less amount of fixatives was required for the mediation of the dye fixation. However, since the molecular structure of this dye is unknown this hypothesis was not confirmed.

Table 6. 20 - Colorimetric and spectral data acquired for Cartasol Blue 3R-EU coloured samples, for different fixative loads after UHP treatment.

Cartasol Blue 3R-EU							
Dye load	Fixative loads	*K/S* (λ_{max})	L*	a*	b*	Colour	OFL UHP
3% (w_{dye}/w_{pulp})	1	0.21±0.002	81.66±0.13	0.50±0.02	-12.96± 0.12		2
	2	2.16±0.02	51.39±0.11	11.24±0.06	-21.43±0.08		
	3	1.40±0.02	57.81±0.15	9.31±0.09	-23.64±0.08		
	4	1.31±0.01	59.68±0.08	9.56±0.03	-23.30±0.05		
	5	1.25±0.004	60.38±0.05	9.55±0.04	-23.18±0.05		
	6	1.15±0.02	61.57±0.20	9.80±0.07	-23.02±0.11		

Table 6. 21 - Comparison between colorimetric and spectral data for Cartasol Blue 3R-EU coloured samples, without UHP and with UHP treatment.

Cartasol Blue 3R-EU							
OFL	*K/S* (λ_{max})	L*	a*	b*	Colour	Δ(*K/S*$_{max}$)%	ΔE
OFL without UHP **4**	1.67±0.02	56.08±0.14	9.33±0.04	-23.25±0.11		+29.3	5.38
OFL with UHP **2**	2.16±0.02	51.39±0.11	11.24±0.06	-21.43±0.08			

The bleedfastness was also accessed and did not show significant variations on the tested samples (Table D.3, Appendices).

iv) Pergasol Violet BN-TKZ

Pergasol Violet BN-TKZ was the next examined liquid dye. The results obtained are depicted in Tables 6.22 and 6.23. As regards the determination of OFL after UHP treatment, the result was the same as without UHP (load no. 2).

Table 6. 22 - Colorimetric and spectral data acquired for Pergasol Violet BN-TKZ coloured samples, for different fixative load for OFL with UHP determination.

Pergasol Violet BN-TKZ							
Dye load	Fixative loads	*K/S* (λ_{max})	L*	a*	b*	Colour	OFL UHP
3% (w_{dye}/w_{pulp})	1	0.76±0.007	68.69±0.14	11.49±0.08	-24.81±0.17		2
	2	2.57±0.014	48.76±0.08	17.04±0.15	-18.34±0.11		
	3	2.06±0.062	53.60±0.41	20.98±0.12	-20.37±0.10		
	4	1.68±0.0106	56.68±0.07	20.50±0.15	-21.05±0.11		
	5	1.66±0.019	56.94±0.14	20.42±0.10	-21.53±0.13		
	6	1.60±0.0115	57.45±0.12	20.26±0.07	-21.13±0.13		

As regards samples treated with and without UHP treatment (Table 6. 23), samples treated with UHP treatment displayed higher *K/S* values. Also, the colour difference, ΔE, of both samples was higher than 1, in the range of minimal difference perceivable by experienced observers.

Table 6. 23 - Comparison between colorimetric and spectral data for Pergasol Violet BN-TKZ coloured samples, without UHP and with UHP.

Pergasol Violet BN-TKZ							
OFL	*K/S* (λ_{max})	L*	a*	b*	Colour	Δ(K/S_{max})%	ΔE
OFL without UHP 2	2.37±0.03	49.98±0.17	16.49±0.09	-18.02±0.03		+8.5	1.38
OFL with UHP 2	2.57±0.014	48.76±0.08	17.04±0.15	-18.34±0.11			

The bleedfastness tests of coloured pulps subjected and non-subjected to UHP revealed non-significant variations (Table D.4, Appendices).

The results obtained with Pergasol Violet BN-TKZ suggest that the preferential adsorption of fixatives (due to its high affinity towards cellulose) may not occur. Possibly, both dye and fixative, are adsorbed on fibres equally and hence no shift on the OFL was observed, with and without UHP treatment of pulp. The only difference was apparently the

enhanced ability of both compounds to diffuse into the fibres, induced by UHP treatment. Hence, UHP, although in a small and not very significant way, promoted an increase on the dye fixation on fibres, without compromising the equilibrium between dye-fixative-cellulose.

v) Pergasol Red 2G-Z

To conclude, Pergasol Red 2G-Z coloured samples were analysed at different levels of fixative loads (Table 6. 24). Similarly to Pergasol Violet BN-TKZ, Pergasol Reg 2G-Z also exhibited the same OFL with and without UHP, as depicted in Table 6. 24, considering the highest *K/S* value.

Table 6. 24 - Colorimetric and spectral data acquired for Pergasol Red 2G-Z coloured samples, for different fixative loads after UHP treatment.

Pergasol Red 2G-Z							
Dye load	Fixative loads	*K/S* (λ_{max})	L*	a*	b*	Colour	OFL UHP
3% (w_{dye}/w_{pulp})	1	0.23±0.002	84.45±0.25	20.19±0.21	2.07±0.42		2
	2	1.83±0.02	63.35±0.11	40.44±0.09	14.41±0.07		
	3	1.44±0.01	67.77±0.04	40.29±0.26	12.50±0.10		
	4	1.28±0.008	69.03±0.07	39.24±0.15	11.74±0.09		
	5	1.25±0.002	69.4±0.05	39.01±0.08	11.56±0.01		
	6	1.15±0.017	69.83±0.08	37.32±0.47	10.78±0.22		

In contrast to Pergasol Violet BN-TKZ, Pergasol Red 2G-Z displayed a higher *K/S* of OFL without UHP samples than that after UHP treatment. Also the colour difference, ΔE, was superior to 2, i.e. in the range of perceivable colour difference (lighter shade). Therefore, UHP have affected the dyeing process negatively.

As discussed before, each dye features interfere with the dyeing process (its structure, affinity and substantivity). It is thus possible that this dye may be rather sensible to fixative concentration in solution and, therefore, shifts on fixative concentration in solution, upon UHP, may promote the dye dispersion in solution, instead of dye diffusion and fixation on the fibre surface.

Table 6. 25 - Comparison between colorimetric and spectral data for Pergasol Red 2G-Z coloured samples, without UHP and with UHP treatment.

Pergasol Red 2G-Z							
OFL	*K/S* (λ_{max})	L*	a*	b*	Colour	$\Delta(K/S_{max})$%	ΔE
OFL without UHP 2	2.14±0.03	61.9±0.06	42.01±0.39	16.06±0.28		-14.5	2.70
OFL with UHP 2	1.83±0.02	63.35±0.11	40.44±0.09	14.41±0.07			

For Pergasol Red 2G-Z, bleedfatsness tests were also performed, and similarly to the previous dyes no significant variations were observed (Table D.5, Appendices).

6.3.2.4. Saving of dyes

Pergasol Red 7BE was selected as a case study to evaluate if UHP could provide dye savings. Hence, tests were performed with Pergasol Red 7BE, resorting to OFL with and without UHP treatment, at 3% (w_{dye}/w_{pulp}) and 4% (w_{dye}/w_{pulp}) dye concentrations. These tests aimed to evaluate the fixation ability of UHP towards the dye and the potential dye savings (which are rather expensive). The results obtained in terms of *K/S*, and colour space data are shown in Table 6. 26. It was found that the colour intensity of 4% (w/w) of dye concentration, without UHP was similar to that obtained with 3% (w_{dye}/w_{pulp}) of dye concentration after UHP treatment. These results revealed that UHP enabled an improved/enhanced dye fixation, able to match or approach the colour intensity of a sample produced with a superior dye load. Even though the shift on fixative agent load from no. 4 (2.5% (w/w) fixative) to no. 6 (3.5% (w/w), due to UHP effect (ca. 40% extra fixative agent), the results achieved showed ca. 33% of dye savings, which is much more expensive than a fixative agent.

These result evidenced a possibility of dyes savings while subjecting pulp to UHP treatment.

Table 6. 26 – Comparison between samples impregnated with 3 and 4% (w/w) load of Pergasol Ref 7BE, with and without UHP.

Pergasol Red 7BE							
Sample		K/S (λ_{max})	L*	a*	b*	Colour	ΔE
4% (w_{dye}/w_{pulp})	without UHP	3.21±0.23	51.74±0.78	39.15±0.72	-2.71±0.29		-
3% (w_{dye}/w_{pulp})	without UHP	2.12±0.04	57.03±0.22	35.36±0.39	-4.85±0.11		6.85
	with UHP	3.15±0.02	53.58±0.07	39.91±0.18	-3.60±0.05		2.18

*data considering the OFL with and without UHP

6.4. Conclusions

The achieved results allowed to conclude that, overall, UHP enabled an improved fixation of dyes on fibres. The positive effect of UHP must be related to the improved accessibility of cellulose in pulp and decreasing of its electrokinetic potential (zeta potential). At the same time, it was verified that different dyes, displayed different sorption behaviours, which were further enhanced upon UHP treatment. It was suggested that these differences could be related to i) chemical structure of dye molecules, ii) dyes affinity and substantivity, iii) variations of cationic fixative concentration, and iv) the influence of UHP on the dye-fixative-cellulose equilibrium. However, it was not possible to prove or confirm the phenomena involved due to the lacking of information on each dye structures. Anyway, the optimum fixative loads were specific for each dye studied and apparently related to the balance between it sorption on the fibres and the interaction with dyes, thus forming charged micelles dispersed in the stock.

It was also confirmed that UHP treatment of pulp allows dyes savings at the same level of colour intensity acquired by fibres.

6.5. References

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Chapter VII

Effect of ultra-high pressure on the impregnation of additives

- Humectants

Contents

7.1. Introduction

Tissue paper is a common good extensively used by modern societies. Tissue products include items such as paper towels, facial tissues or toilet paper, easily found in any small or big groceries store. Due to its end purposes, it is easy to recognized two main physical attributes of these products, softness and their absorbency, with especial emphasis on absorbency. The particular challenge in papermaking has been to appropriately balance these various properties to provide superior tissue paper. [1–4]

Tissue papers and towelling grades that require good absorbency also require suitable strength properties to maintain their structural integrity. Although often becomes difficult to balance both, since both requirements tend to conflict.[5] Although somewhat desirable for towel products, softness is particularly important property for facial and toilet tissues. [3]

Softness is the tactile sensation perceived by the consumer who holds a particular paper product, rubs it across the skin, and crumbles it within the hand. Such tactile perceivable softness can be characterized by, but is not limited to, friction flexibility and smoothness, as well as subjective descriptor, such as feeling like velvet, silk or flannel. This tactile sensation is a combination of several physical properties, including the flexibility or stiffness of the sheet of paper, the frictional properties of the web, as well as the texture of the surface of the paper.[1,3,4,6]

Absorbency is the measure of the ability of a certain material to absorb liquids. Overall absorbency as perceived by consumers is generally considered to be a combination of the total quantity of liquid a given mass of tissue will absorb at saturation as well as the rate at which the mass absorbs the liquid. Absorption can be directly related to the softness and bulk, although not always in the same way. Due to paper's affinity for water, paper is an absorbent product, the fibres form hydrogen bonds with water. But paper with many links between fibres has more resistance to water absorption. This is because there are more links between fibres, which makes it less porous, preventing the diffusion of water inside. Besides, water penetration must break some links between fibres, delaying the penetration itself. [1,3,7]

The creping in tissue paper is a key operation to improve absorption. During the drying operation the sheet adheres to a large dryer called Yankee. When the paper reaches the end of the course, once it has been dried, strikes against a blade which causes the paper to crinkle, developing microwrinkles. In this operation many bonds between fibres that had been formed during the drying stage, are broken generating a lot of fines, which are

capable of absorbing water. It also increases expressively the surface area of the sheet, facilitating the interaction with water. Finally, the creping increases the bulk and makes the paper soft. Therefore, the creping operation is an essential procedure for tissue paper production.[4,6,8–10]

In hygiene and cosmetic products, chemical additives, otherwise denominated as wetting agents, humectants or moisturizers may be added to further improve both absorptive properties along with softness properties. [11] In products such as tissue paper or non-woven fabrics its composition includes at least one kind of materials selected from salts having high hygroscopy, or polymer having high hygroscopy. Such chemical materials are preferably chosen from food additives (e.g. polyphosphates), or cosmetic ingredients (e.g. glycerine, pyrrodilone, polyethylene glycol, etc.).[11–14] These chemicals act by attracting and holding on to water. Thus these compounds are applied, in a wide variety of products, either to retard water loss or to increase its uptake. A good example would be their use to improve moisture content on tissue paper, by capturing and retaining moisture in air, and enhance softness and its feel to skin. [11]

Ultra-high pressure (UHP) is a technology that has demonstrated its benefits towards reversing hornification (responsible for fibres stiffening and losses on hydration), due to the structural changes it produces. Besides the rearrangements of crystalline regions, it induces forced hydration on amorphous regions provoking water molecules to be imprisonment in less accessible sites as strongly bound water. This also provokes fibril disaggregation and improved accessibility.[15] This enables higher accessibility towards chemicals and enzymes, as demonstrated in the literature.[15–17] With this in mind, the work aimed to use UHP to promote the impregnation of humectants on fibres to improve its hydrophilic features and thus enhance fibres absorbency. It is also expected that by improving moisture capture, the addition of this additives may confer a certain freshness and softness to the touch of pulp, although this features will not be considered on this study.

7.2. Materials and Methods

Similarly to previous studies on the impregnation of additives, for the reasons already described, the raw material used in these studies was virgin hardwood pulp. Therefore, *Eucalyptus globulus* bleached *kraft* industrial pulp, ***E***, kindly supplied by Renova FPA, S.A. was used as reference raw material for the impregnation studies. Also the humectants employed were the following:

- Polyethylene glycol, Mw 200, PEG 200, (99.5%, Acros Organics)
- Polyethylene glycol Mw 400, PEG 400 (99%, Acros Organics)
- Polyethylene glycol Mw 600, PEG 600 (99.5%, Acros Organics)
- Sodium polyphosphate, PP (pure, Acros Organics)

7.2.1. Impregnation of pulp with saturated humectant solutions

The impregnation of PEG 200 on ***E*** pulp was performed as follows: 10 g of pulp were dispersed in water and then PEG 200 was added reaching a total volume of 440 mL containing 20% (w/v) PEG concentration. These doped pulp samples were prepared by two different ways. One was by subjecting samples to UHP treatment (500 MPa for 10 min, optimum conditions, previously used on dyes impregnation tests), while the other was by subjecting samples to stirring, only, for the same time.

Samples treated by UHP treatment were placed, beforehand, on HDPE flasks, vacuum sealed, and then subjected to UHP. The UHP treatments were performed on a high pressure apparatus, model 55 Hyperbaric, with water as pressure transmission medium.

Samples treated and untreated by UHP were then filtered with glass porous filters (previously weighted), allowed to dry and then placed in a desiccator over P_2O_5 to achieve nearly zero moisture content. Afterwards samples were weighted and the shifts on samples weights were analysed. The same procedure was used for the impregnation of pulp with PEG 400 and PEG 600. Being the only difference the PEG 600 concentration, which was 10% (w/v). It is noteworthy that the use of a PEG 600 solution with 10% (w/v) of concentration, instead of a solution with a concentration of 20% (w/v) (for comparative reasons), was due to difficulties on the solubilisation of PEG 600 in water and its relatively high viscosity.

Additionally, the same procedure was applied on the impregnation of pulp with PP, being the only difference the impregnation solution concentration, which was 5% (w/v).

7.2.2. Impregnation of pulp with selected humectants

The same impregnation procedure was carried out, as in section **7.2.1**., for the following sets of pulp samples, impregnated with 5% (w/v) PEG400, 1% (w/v) PEG400, 5% (w/v) PP, 1% (w/v) PP and mixture of 0.5% (w/v) PEG with 0.5% (w/v) PP.

7.2.3. Leaching tests

The leaching of additives from impregnated pulp samples was accessed according to the procedure described below. 1 g of each sample prepared as described in section **7.2.1**, was weighted (in duplicate) and placed in 100mL of distilled water under stirring at room temperature. Aliquots were collected from time to time and analysed for released additives. PEG samples were analysed by high performance liquid chromatography, HPLC, and PP samples by orthophosphate content in solution.

7.2.3.1. Quantification by High performance liquid chromatography (HPLC)

- Acetonitrile (Acros Organics, 99.9% HPLC grade)
- Ultrapure water

The quantification of PEG polymers was performed on an Acella apparatus from Thermo Scientific, equipped with an autosampler, a reflective index detector (RI) and a diode array detector (PDA). All analyses were carried out with a HypersilGold column, from Thermo Scientific, with dimensions 50x2.1mm, particle size of 1.9 μm and pore size of 175 Å.

In case of PEG 200, analyses were performed using isocratic conditions (4% acetonitrile: 96% water), with a 350 μL/min flow rate, and an injection volume of 10 mL. Data was analysed considering PDA results at 190 nm. Calibration was performed considering solution of 0.1, 0.4, 0.8 and 1% (w/v), and is represented in Appendices E.

As concerns PEG 400 and PEG 600, its quantification was performed also under isocratic condition (20% acetonitrile, 80% water), with a flowrate of 300 μL/min, and an injection volume of 10 mL. Data was analysed considering PDA results at 194 nm. The calibration curves for PEG 400 and PEG 600 quantification was performed considering standard solutions of 0.25, 0.5, 0.6, 0.75, 1.2 %(w/v) and 0.1, 0.25, 0.5, 0.75 and 1% (w/v), respectively. These calibration curves are also presented in Appendices E.

7.2.3.2. Colorimetric quantification of orthophosphates

- H_2SO_4 (Acros Organics, 96%)
- Antimony potassium tartrate (99%, Acros Organics)

- Ammonium molybdate (99.9%, Acros Organics)
- Ascorbic acid (99%, Acros Organics,)
- Ammonium Persulphate (99%, Alpha aesar)
- KH_2PO_4 (99%, WRV)
- NaOH (85%, VWR)

The amount of released PP was followed considering the amount of total orthophosphates in solution, in agreement with norm EPA 3652. The process is based on ammonium molybdate and antimony potassium tartrate reaction in acid medium with dilute solution of phosphorous to form antimony-phospho-molybdate complexes. These complexes are reduced to intensely blue coloured complexes by ascorbic acid, being the colour proportional to the phosphorus concentration.

Before quantification, according to the norm, a combined reagent required for the tests was prepared. This reactant enables the quantification of orthophosphates. With this purpose the following solutions were prepared, H_2SO_4 5 N, antimony potassium tartrate solution (1.3715 g $K(SbO)C_4H_4O \cdot 1/2H_2O$ in 500 mL), ammonium molybdate solution (20 g of $(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$ in 500 mL distilled water) and ascorbic acid 1 M. For the combined reagent preparation, 50 mL of H_2SO_4 5 N were placed on a beaker under constant stirring. Then, by order, the following solutions were added, 5 mL of antimony potassium tartrate solution, 15mL of ammonium molybdate solution and 30 mL of ascorbic acid solution. The combined reagent was then stored to use on the next steps.

The quantification of the total of orthophosphates from each sample was determined in agreement with procedure described below. Initially, 50 mL of sample (1 mL aliquots were diluted up to 50 mL) was placed on 100-150 mL beakers, along with 1 mL of H_2SO_4 5.5 M and 0.4 g of ammonium persulphate. The mixture was allowed to boil until volume was reduced to approximately 10 mL. After cooling down, samples were diluted up to 25-30 mL and its pH was tuned to 7.0 ± 0.2 with NaOH solutions (10, 1, 0.1, 0.01 and 0.001 M) using a pH Meter, model HI2020 - edge® multiparameter, from Hanna Instruments. Then, samples were transferred into a 50 mL volumetric flask, to which 8 mL of combined reagent were also added. The flasks were then filled with distilled water up to 50 mL. After 10 min waiting, samples absorbance was measured on UV-vis spectrophotometer Evolution 220 (Thermo Scientific) at 880 nm.

For the preparation of the blank sample, used as reference, the procedure was the same, being the only difference the substitution of sample for distilled water.

Calibration was performed by analysing standard solutions of KH_2PO_4 between 0.3 mg/L and 1 mg/L. The calibration curve is represented in Appendice E.

7.2.4. Moisture uptake

All samples were investigated for its ability to uptake moisture at room conditions. For that 1g of each sample (absolutely dry) was placed on previously weighted petri plates (in duplicate). These were then left at room temperature and at ca. 50% relative humidity (RH), until constant weight. The moisture uptake of each samples was then determined based on equation 6.1.

$$X_{eq} = \frac{m_{final} - m_{initial}}{m_{initial}} \times 100 \qquad \text{Equation 6. 1}$$

7.2.5. Handsheet formation

Handsheets from samples impregnated with the selected humectants, were prepared following ISO 5269-2:2004, in a Rapid-Köthen sheet former (Karl Schröder KG).

7.2.6. Physical and Mechanical Properties

Fibres drainability was examined according to ISO 5267-1:1999. The paper handsheets thickness, density and specific volume was evaluated according with ISO 534:2011. Furthermore, tensile strength, stretch%, tear index, burst index, air resistance (Gurley method), capillary rise and water absorption capacity were evaluated in every sample according to, ISO 1924-2:2008, ISO 1974:2012, ISO 2758:2014, ISO 5636-5:2003, ISO 8787:1986 and ISO 12625-8:2010, respectively.

7.3. Results and Discussion

The main purposes on this chapter was to test different humectants that would convey cellulose its hygroscopic abilities, to enhance pulp hydrophilicity and thus improve pulp sorption abilities. It may be proposed that while gaining an improved ability to capture moisture, the softness of pulp would be also improved.

7.3.1. Tests on different humectants

Preliminary impregnation tests were performed with different humectants to access pulp properties influenced by the presence of these reactants, and to check the UHP treatment effect on these properties. Thus, the following additives were tested: sodium polyphosphate (PP) and polyethylene glycol (PEG) with different molecular weights, M_w 200(PEG 200), M_w 400 (PEG 400) and M_w 600 (PEG 600). The same bleached *E. globulus* pulp (***E***) as used in previous chapters, was employed on these studies. Pulp ***E*** was impregnated with 20% (w/v) solutions (PEG 200 or 400), 10% (w/v) of PEG 600, or 5% (w/v) of PP. A part of this samples were subjected to UHP treatment, while the other was subjected to stirring only. For simplicity, samples were designated as shown in Table 7. 1.

Table 7. 1 – Designations of pulp samples impregnated by PEG and sodium polyphosphate.

Sample	Description
E	Industrial Bleached kraft *E. globulus* pulp
PEG200	***E*** impregnated with a 20% (w/v) PEG 200 solution without UHP treatment, just stirring.
PEG200 HP	***E*** impregnated with a 20% (w/v) PEG 200 solution by UHP treatment.
PEG400	***E*** impregnated with a 20% (w/v) PEG 400 solution without UHP treatment, just stirring.
PEG400 HP	**E** impregnated with a 20% (w/v) PEG 400 solution with UHP treatment.
PEG600	***E*** impregnated with a 10% (w/v) PEG 600 solution without UHP treatment, just stirring.
PEG600 HP	***E*** impregnated with a 10% (w/v) PEG 600 solution with UHP treatment.
PP	***E*** impregnated with a 5% (w/v) PP solution without UHP treatment, just stirring.
PP HP	***E*** impregnated with a 5% (w/v) PP solution with UHP treatment.

7.3.1.1. Additives retention on fibres

The fixation of additives onto fibres was investigated by monitoring changes of samples weights (before and after impregnation, of dried samples) and also by analyses of filtrates. The results obtained are presented in Table 7. 2 for samples impregnated with PEGs and in Table 7. 3 for samples impregnated with PP.

Based on weight increment of samples impregnated with saturated PEG solutions, before and after the UHP treatment, it was possible to infer that UHP prompted an enhanced impregnation of additives to fibres, rendering their increased retention on fibres

(Table 7. 2). As discussed in previous chapters, UHP enables an improvement of fibres accessibility towards chemicals. Hence, similar behaviour was detected in the study with some PEGs solutions. The monitoring of filtrates was also performed for control. However, these results are not portrayed here, due to divergences found in results, most likely related with high relative errors obtained in dilutions required to enable filtrates analysis.

Table 7. 2 – Increments of weight of pulps impregnated with PEG solutions, with and without UHP treatment.

Samples	PEG200	PEG200 HP	PEG400	PEG400 HP	PEG600	PEG600 HP
$w_{dry\ pulp}(g)$	9.1861	9.1852	9.1753	9.2113	9.2014	9.1712
$w_{dry\ impregnated\ pulp}(g)$	15.2428	15.3047	13.4593	16.6139	12.3711	13.472
Δ (g)	6.0567	6.1195	4.284	7.4026	2.3149	4.3009
Δw (%)	65.9	66.6	46.7	80.4	34.4	46.9
% $w_{additive}/w_{pulp}$*	39.7	40.0	31.8	44.6	25.6	31.9

*calculated assuming that Δ (g) corresponds to the amount of additive retained

Analysing the experimental data, overall, it was possible to observe, that PEG 400 solution allowed the best retention/fixation, especially upon UHP treatment. The uptakes of PEG 200 and PEG 600 were inferior to that of PEG 400, although the concentration of PEG 600 (10% (w/v)) used was inferior to those for PEG 200 and PEG 400 (20% (w/v)). However, it seems clear that PEG sorption on fibres depended on their molecular weights. This must be related to the PEG capacity to form intermolecular hydrogen bonds and Van-der-Waals bonds with cellulose and with its diffusion inside fibres. UHP enabled an improved diffusion of PEG molecules due to the improved accessibility of fibres, thus enhancing the additives adsorption. Besides the specific interaction of PEG with cellulosic fibres the diffusion inside fibre cell structure also can be the limiting factor. Hence the best results obtained with PEG 400 may be the result of successful combination of both factor.

Samples impregnated with PP were also monitored, and the obtained results are presented in Table 7. 3. In this case the opposite results, relatively to PEG samples, were achieved. Instead of an enhanced sorption of PP, upon UHP treatment, a decrease of adsorbed PP was registered. However, PP sample exhibited higher rigidity when compared to PP HP. Possible explanations may be related to the fact that i) UHP assisted impregnation allowed a more uniform distribution of PP and therefore the relatively small crystals only are precipitated on fibres, more homogenously distributed and possibly strongly hydrated, ii) PP without UHP treatment may have produced heterogeneous nucleation of PP on fibres surface, prompting the formation of larger crystals, heterogeneously distributed, thus conferring more conspicuous rigidity to the sample.

Table 7. 3– Increments of weight of pulps impregnated with PP, with and without UHP treatment.

Samples	PP	PP HP
$w_{dry\ pulp}(g)$	9.2296	9.1842
$w_{dry\ impregnated\ pulp}(g)$	16.1015	14.9257
Δ (g)	6.8719	5.7416
Δw (%)	74.5	62.5
% $w_{additive}/w_{pulp*}$	42.7	38.5

*calculated assuming that Δ (g) corresponds to the amount of additive retained

7.3.1.2. Leaching tests

i) PEG samples

After analysing additives fixation on fibres, upon UHP treatment, its retention upon leaching was also studied. Samples were subjected to 3 h leaching in distilled water, under stirring and at room temperature. Aliquots were collected from time to time and analysed by HPLC for PEG samples and UV-Vis, for orthophosphate content, as regards PP samples.

Results for the different PEG impregnation samples are given in Figure 7. 1. Overall, results revealed a higher release of additives for UHP treated samples, than for those without UHP treatment. As expected UHP treated samples released more additives during leaching relatively to non-treated samples. This result confirms the presence of higher amounts of PEG in pulp, after UHP treatment, than after conventional impregnation.

As concerns PEG 200 impregnated pulp samples, the quantification of PEG 200 release, from both non-treated and UHP treated samples, was performed considering the sum of all molecular fractions (7 fractions), presented in PEG 200 (broad M_w distribution) (Figure 7. 2). The contribution to the leaching of each fraction was also analysed at the end of the 3h leaching period, to perceive which molecular weights were more prone to be leached, or were retained on fibres (Figure 7. 3). Each number of fraction (F1-F7) roughly corresponds to the oligomers (from monomer to heptamers).

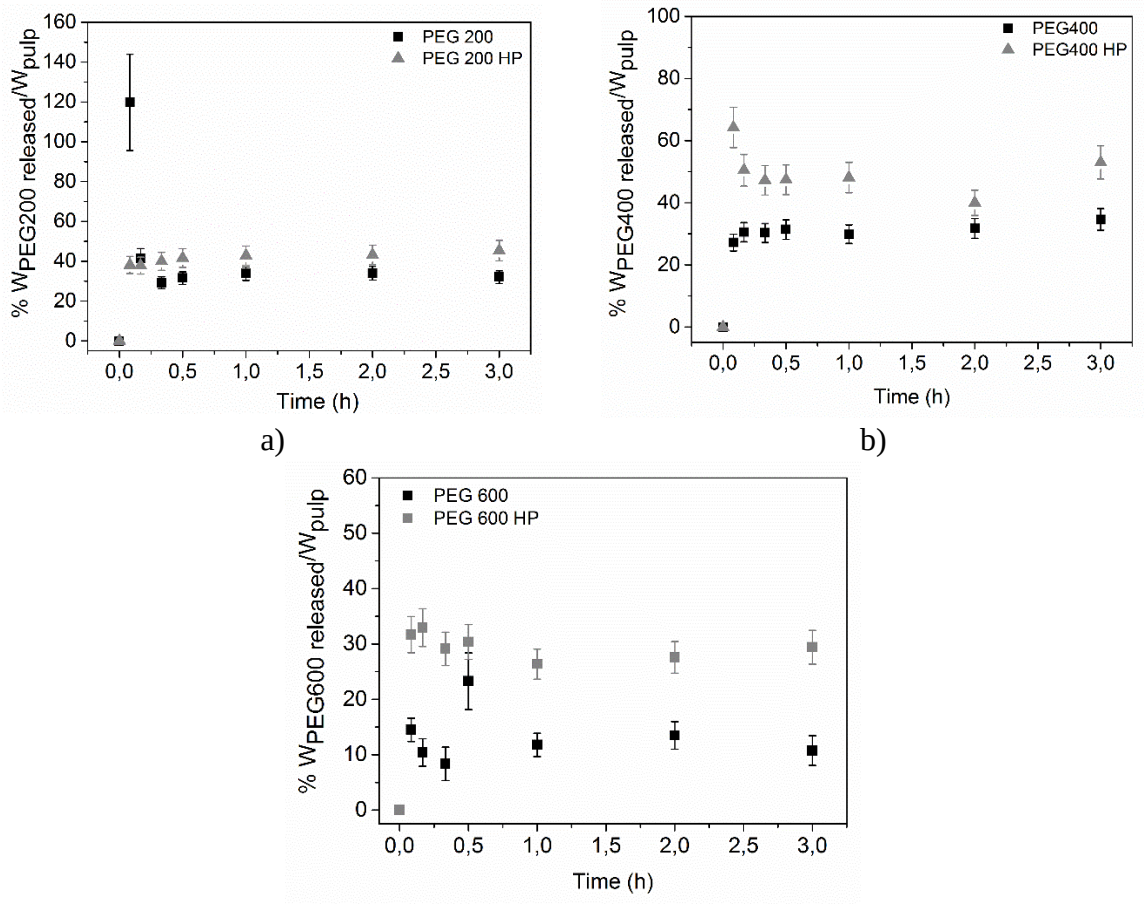

Figure 7. 1 – Leaching of PEG samples, impregnated with and without UHP treatment. a) PEG200 HP and PEG200; b) PEG400 HP and PEG400; c) PEG 600 and PEG600 HP, respectively.

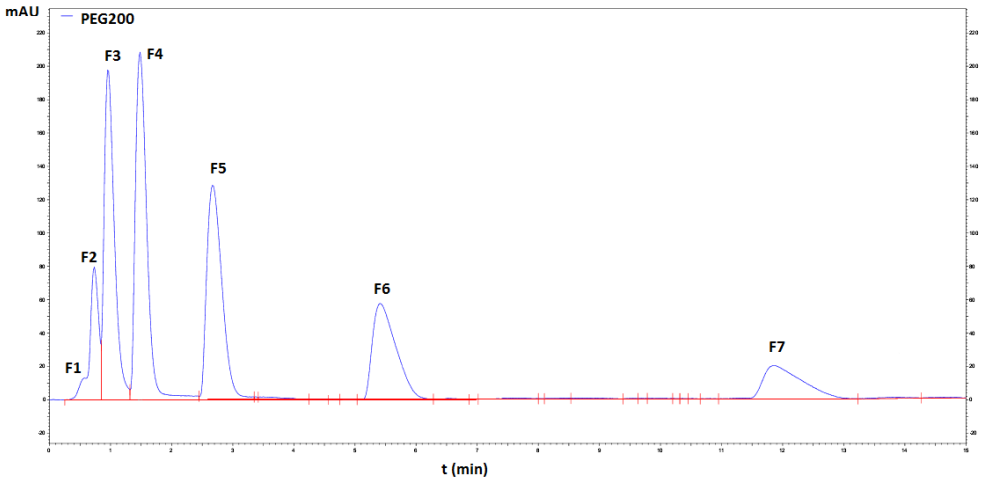

Figure 7. 2 – HPLC chromatogram of PEG200 sample (detection at 190nm), where F1 correspond to the 1st fraction of PEG200 exiting the column, followed by F2 the 2nd fraction, F3 the 3rd fraction, F4 the 4th fraction, F5 the 5th fraction, F6 the 6th fraction and F7 the 7th fraction.

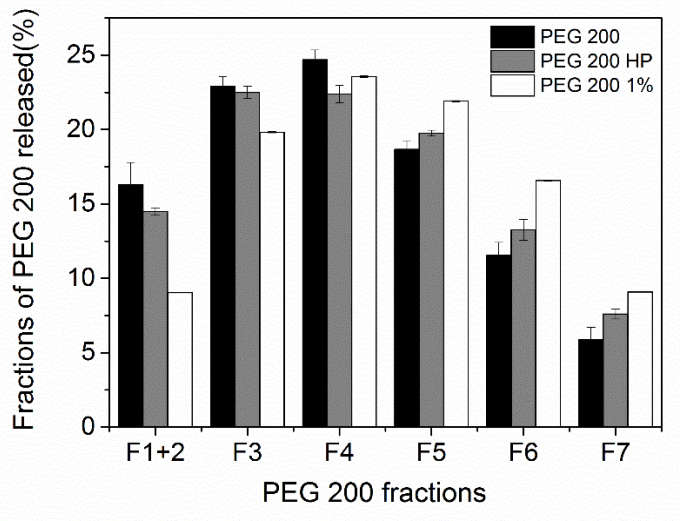

Figure 7. 3 – Leaching of PEG 200 fractions from samples PEG 200 and PEG200 HP, after 3 h leaching period. For comparison, it is also presented the distribution of fractions in a PEG 200 standard solution with 1% (w/v) concentration. The terminology used in Figure 7.2 to designate fractions was the same, although, in this case F1+2 represents fraction 1 and 2.

The results in Figure 7. 3 showed clearly the discrimination effect of different PEG oligomers retention on cellulosic fibres. Relatively small PEG molecules (monomers-dimers) were much easily to release during leaching than the bigger oligomers. PEG molecules from fractions F5-F7 were preferentially retained on fibres during leaching. It can be also concluded that PEG molecules from fractions F5-F7 were easily leached from the pulp samples impregnated with PEG 200, under UHP conditions. This fact may be tentatively explained by the better accessibility of PEG 200 HP sample, than of PEG 200 pulp sample, due to the less hornification during drying. Anyway, the results obtained showed that fibres interaction increases with increased molecular weight of PEG, at least up to heptamers.

This case scenario discrimination effect was only possible to analyse for PEG200 only, because it was the only PEG exhibiting a well-defined molecule weight distribution of oligomers. However, the same study was not possible to carry out for samples impregnated by PEG 400 and PEG 600, because of limited resolution of either HPLC or SEC (size exclusion chromatography) columns to separate individual oligomers.

ii) PP samples

The leaching of PP from samples impregnated with and without UHP, was monitored by analysing content of orthophosphates in solution (Figure 7. 4). The results revealed lower PP release from PP HP sample, relatively to PP pulp sample. Such result was

expected and is in agreement with a lower amount of PP attached to fibres, upon UHP treatment, as was observed from mass balance results (Table 7. 3).

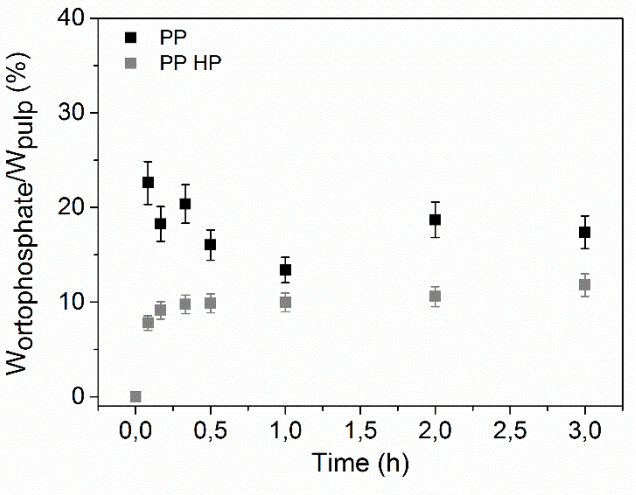

Figure 7. 4 –PP release profiles from PP impregnated pulp samples, with and without UHP treatment (PP HP and PP respectively).

7.3.1.3. Moisture sorption

The capacity of impregnated samples to uptake moisture was also investigated, under room conditions (20±1ºC and ca. 50% RH). The results obtained are shown in Figure 7. 5. The results revealed higher moisture uptake for all samples, comparatively to control pulp (***E***), except for sample PEG 600 HP. This last exhibited a X_{eq} lower than that of untreated pulp (***E***), conversely to PEG 600 sample, whose X_{eq} was higher than ***E***. The remaining samples, all demonstrated higher X_{eq}, which was further boosted upon UHP, up to the double of untreated pulp.

Although samples impregnated with PEG200 exhibited rather promising results, results with PEG 400, after UHP treatment were even more impressive.

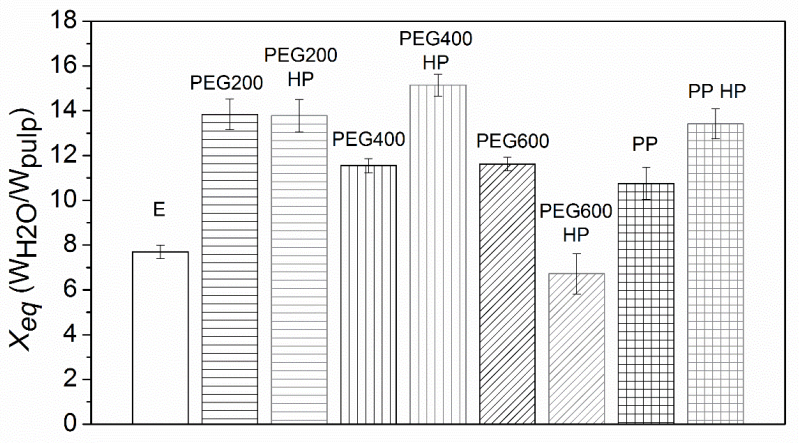

Figure 7. 5 –Moisture uptake, X_{eq} % ($w_{moiture}/w_{dry\ pulp}$), (20±1ºC, ca 50%RH), for PEG and PP series of samples, impregnated with and without UHP treatment.

Moisture uptake results could also be considered as a way to measure the efficiency of additive impregnation. The purpose of humectants on fibres is to provide additional sites for moisture uptake and, therefore, to increase pulp affinity towards water. In the case of the three PEGs, the difference in M_w, between one another, may play an important role, not only on the impregnation efficiency (larger or smaller molecules are impregnated/retained less or more efficiently), but also from the point of view of moisture uptake (larger molecules interacting with cellulose could hinder their moisture uptake by free OH groups).

It is important to select a humectant that allows a good fixation, together with a high capacity to uptake and retain moisture to produce smooth and moistened paper. Since, PEG 400 X_{eq} was almost as elevated as PEG200, together with a good fixation capacity (similar to PEG 600), PEG 400 was selected for further studies.

As concerns samples impregnated with PP, higher X_{eq} was found for UHP treated samples than for untreated ones. Which is inconsistent with the higher amount of additive on fibres. Probably, the fact that PP samples, without UHP, were very rigid, with non-uniform PP distribution on the fibre surface, may explain a difficulty to uptake water. PP was possibly more uniformly distributed and hydrated, on the fibrils surface of pulp, due to UHP treatment, which promoted increased accessible area and high X_{eq}. Nevertheless, for testing other properties, such as physical and mechanical properties, a smaller additive load was considered to avoid abrupt PP precipitation on pulp.

7.3.2. Papermaking properties of pulp impregnated with PEG and PP

After preliminary tests for the pulps impregnation with different PEG and PP, the most advantageous additives, namely PEG 400 and PP, were selected for further evaluation of their effect on papermaking properties of modified pulps. The concentration of humectants in assays were diminished in order to approximate the industrial conditions and due to cost/efficiency reasons. Additionally, it was pertinent to test also the impregnation of mixed additives, namely PEG 400 with PP, to look for possible synergetic effects. The purpose of this study was to understand how these additives affect not only the interaction with water (moisture uptake, capillary rise, water absorption capacity), but also basic paper properties (ºSR, bulk, tensile strength, burst index, stretch%, tear index, air resistance and opacity). Initially the assays were carried out to access and evaluate the materials capability to sorption and then the papermaking properties were accessed.

The designations attributed to each samples are given in Table 7. 4.

Table 7. 4 – Samples designations.

Sample	Description
E	Industrial bleached kraft *E. globulus* pulp
E HP	***E*** treated by UHP treatment
5% PEG400	***E*** impregnated with a 5% (w/v) PEG400 solution
5% PEG400 HP	***E*** impregnated with a 5% (w/v) PEG400 solution under UHP treatment
1% PEG400	***E*** impregnated with a 1% (w/v) PEG400 solution
1% PEG400 HP	***E*** impregnated with a 1% (w/v) PEG400 solution under UHP treatment
5% PP	***E*** impregnated with a 5% (w/v) PP solution
5% PP HP	***E*** impregnated with a 5% (w/v) PP solution under UHP treatment
1% PP	***E*** impregnated with a 1% (w/v) PP solution
1% PP HP	***E*** impregnated with a 1% (w/v) PP solution under UHP treatment
Mixture	***E*** impregnated with a mixture of 0.5% (w/v)+0.5% (w/v) of PEG400 and PP
Mixture HP	***E*** impregnated with a mixture of 0.5% (w/v)+0.5% (w/v) of PEG400 and PP, under UHP treatment

7.3.2.1. Water sorption

The water sorption was evaluated for all samples, by moisture sorption tests (20±1ºC and ca. 49% RH), capillary rise tests and water absorption capacity tests (basket immersion test).

The moisture uptake of all samples impregnated with humectants (Figure 7. 6), with and without UHP treatment, exhibited a significant increase of X_{eq}, relatively to the control pulp (***E***). The highest water sorption was registered for samples treaded with 5% (/w/v) PP, especially under UHP conditions. Samples impregnated with 5% PP revealed the highest water sorption, even higher than with samples impregnated with 5% (w/v) PEG400, whose levels of water uptake were similar to those obtained with samples impregnated with 1% PP (w/v). Samples impregnated with 1% (w/v) PP were those with the highest water sorption, when compared to PEG samples. Among samples treated with and without UHP, it was possible to observe that only samples 5% PEG400 HP and Mixture HP revealed a lower X_{eq}, in relation with untreated samples (5% PEG 400 and Mixture, respectively). This divergence could be explained by the experimental error.

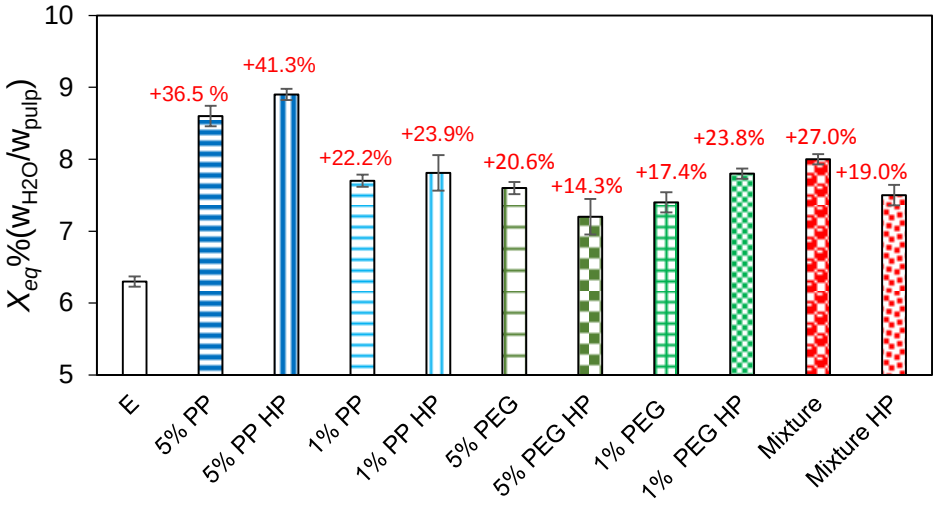

Figure 7. 6 – Moisture uptake, (20±1ºC; 50% RH), for samples impregnated with PEG 400, PP, and their mixture (0.5% PEG+0.5% PP), with and without UHP treatment.

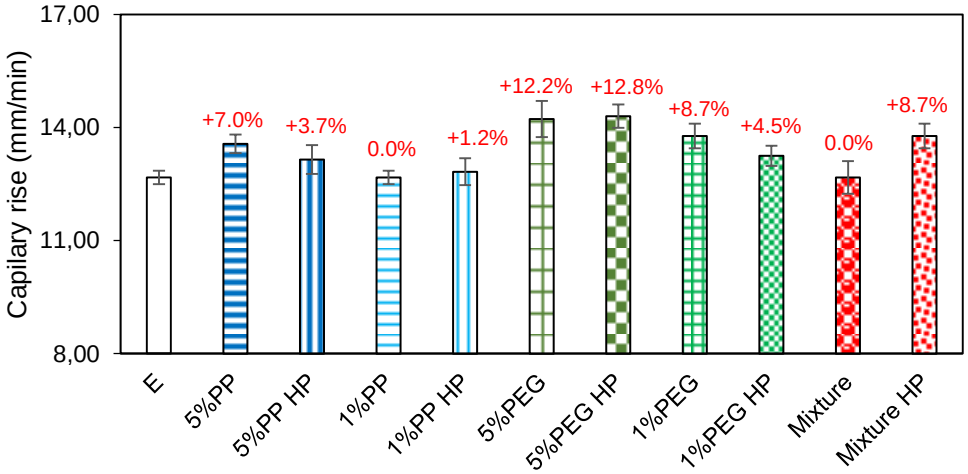

Figure 7. 7 – Capillary rise results of pulp samples impregnated with PEG 400, PP and their mixture (0.5% PEG+0.5% PP), with and without UHP treatment.

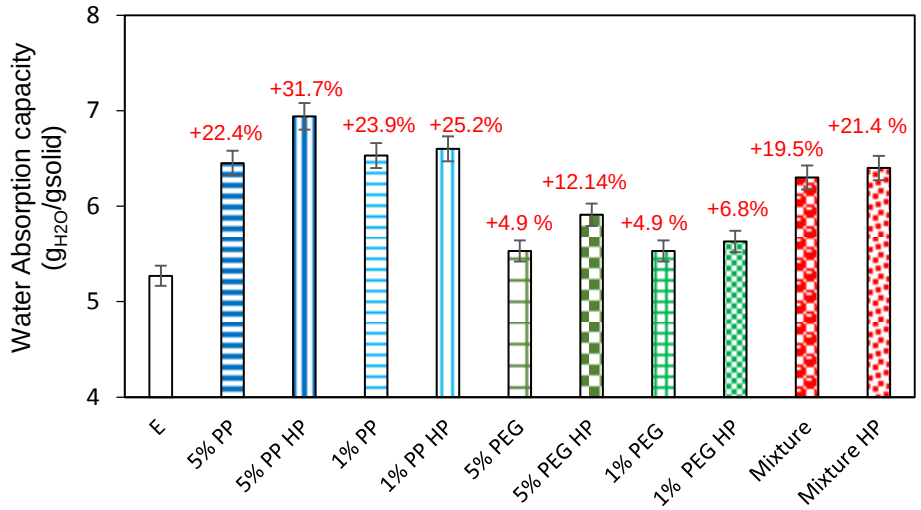

Figure 7. 8 - Water absorption capacity of samples impregnated with PEG 400, PP and their mixture (0.5% PEG+0.5% PP), with and without UHP treatment.

The moisture uptake assays were further complemented with Klemm capillary tests, and water absorption capacity tests, typically used in Renova mill to scrutinize the pulps hydration skills. It was found that not always samples impregnated upon UHP resulted on increased capillarity, and that results were somehow divergent between one another. Overall, the impregnation with humectants showed similar or some increased capillarity of pulp (Figure 7. 7). This was expectable due to the addition of hydrophilic additives to fibres. However, in case of UHP treated samples, results diverged between one another. In some cases, UHP slightly improved capillarity (1% PP HP, 5% PEG HP and Mixture HP), while in other cases this one was reduce (5% PP HP and 1% PEG HP). A possible explanation is related to the eventual balance between improved hydrophilicity of fibres and the final macroporosity, affected by pulp modification.

The water absorption capacity (Figure 7. 8) is a standard procedure in Renova mill to acess papers hydration skills. The results achieved revealed that all UHP treated samples exhibited higher water absorption capacity, than untreated ones. This was not always in agreement with moisture sorption tests (Figure 7. 6). Though the divergences were minimal. It is noteworthy that 1% PP sample (with and without UHP treatment) demonstrated the same level of sorption as 5% PP (without UHP), and these results are not far from samples treated with a mixture of both PEG and PP.

The evaluation of samples hydration skills, demonstrated that the use of humectants to improve fibres hygroscopicity gave positive results, with special emphasis for samples impregnated with 5% PP, followed by 1% PP and mixture of PEG with PP. Practically in all assays the hydration properties inserted by humectants were enhanced by UHP treatment, though not always very significantly.

7.3.2.2. Physical and Mechanical properties of modified pulps

Physical and mechanical properties were studied using unbeaten pulps. All samples were tested and its basic indices were examined (drainability, bulk, burst index, tensile strength, stretch %, tear index, air resistance and opacity).

i) Pulps doped with PEG

The results obtained for samples impregnated with PEG are presented in Table 7. 5. Results on non impregnated pulp, treated with and without UHP (***E*** and ***EHP***) are also depicted for comparative reasons and the differences in physical parameters are expressed with respect to reference pulp ***E***.

Table 7. 5 – Physical and mechanical properties of pulp impregnated with and without PEG 400, with and without UHP.

	E	EHP	Δ %*	5% PEG	Δ %*	5% PEG HP	Δ %*	1% PEG	Δ %*	1% PEG HP	Δ %*
°SR ±0.9	17	16	-5.9	17	0	18	+5.9	19	+11.8	18	+5.9
Bulk, cm^3/g ± 0.10	2.030	2.077	+4.7	2.138	+5.3	2.131	+5.0	2.147	+5.8	2.094	+3.2
Burst index, $KPa.m^2/g$ ±0.08	1.03	1.10	+6.8	0.57	-44.7	0.64	-37.9	0.92	-10.7	1.00	-3.1
Tensile strength, N.m/g ±1.17	23.5	22.5	-4.3	14.7	-37.4	17.0	-27.7	20.8	-11.5	21.7	-7.7
Stretch, % ±0.06	1.19	0.93	-21.8	0.70	-49.0	0.86	-27.7	1.02	-14.3	1.20	+0.8
Tear index, $mN.m^2/g$ ± 0.18	3.58	4.38	+22.3	2.53	-29.3	2.48	-30.7	3.74	+4.5	3.68	+2.8
Opacity, % ±1.1	84.26	84.28	+0.02	84.64	+0.45	84.92	+0.78	83.39	-1.0	83.92	-0.4
Air resistance, s/100mL ±0.05	1.19	1.03	-13.4	0.72	-39.5	0.75	-37.0	1.28	+7.6	1.24	+4.2

***** The increment of strength properties after impregnation, with or without, UHP pre-treatment were calculated with respect to pulp **E** (Δ %).

It was found that the impregnation of fibres with PEG diminished the strength of paper (decreases on tensile strength, burst and tear index). In the case of pulp samples impregnated with the highest load of PEG, this loss on strength properties was the highest, relatively to samples impregnated with lower PEG loads. However, this deterioration of strength properties was always diminished, while UHP processing of pulp was applied in the impregnation assays with humectants.

Samples impregnated with 5% (w/v) PEG contained a higher amount of PEG400, comparatively with samples treated with 1% (w/v) PEG. In this case PEG should play a role of debonding agent, which contributes for an easier disruption of fibres network (losses on strength properties).[7,18–20] Although UHP treatment benefits the improvement of paper strength, the losses in mechanical properties were still significant when compared to initial pulp (***E***).

Decreasing PEG load, although it resulted in small losses on water uptake abilities, it allowed to reduce the impact of PEG on fibres strength properties. Nevertheless, fibres impregnated with UHP treatment were able, not only to reduce remarkably the interference brought by PEG on fibres strength properties, but also, in some cases, to improve in small percentages those properties. It is possible that the decrease of PEG load, together with UHP treatment effects may have contributed to keep or even improve, somehow, fibre interbonding. This fact is endorsed by air resistance results. An increased PEG load, even upon UHP, rendered lower air resistance, which suggests higher porosity, whereas in case of samples treated with low amount of PEG (1% (w/v)), fibres become more strongly

linked and organized, as demonstrated by the increase on handsheets air resistance. Besides, adding PEG to fibres rendered and increased higher bulk.

Even though the undesirable effect brought by PEG it was possible to improve fibres water uptake, without harm significantly strength properties. Using a moderate PEG concentration (1% (w/v)) it was possible to reach fairly good water absorptivity (Figure 7. 6 – 7.8), without serious deterioration of mechanical strength (Table 7. 5).

ii) Pulps doped with PP

Samples impregnated with PP were also investigated according to its basic paper properties, which are presented in Table 7. 6.

Table 7. 6 - Physical and mechanical properties of pulp impregnated with and without PP, with and without UHP.

	E	EHP	Δ %*	5%PP	Δ %*	5%PP HP	Δ %*	1%PP	Δ %*	1%PP HP	Δ %*
ºSR ±0.9	17	16	-5.9	15	-11.8	16	-5.9	16	-5.9	17	0
Bulk, cm^3/g ± 0.10	2,030	2,077	+4.7	2,122	+4.5	2,102	+3.5	2,056	+1.3	2,040	+0.5
Burst index, $KPa.m^2/g$ ±0.08	1,03	1,10	+6.8	0,67	-35.0	0,70	-32.0	1,28	+24.3	1,39	+35.0
Tensile strength, N.m/g ±1.17	23,5	22,5	-4.3	17,5	-25.5	17,5	-25.5	25,3	+7.7	28,1	+19.6
Stretch, % ±0.06	1,19	0,93	-21.8	0,89	-25.2	0,84	-29.4	1,19	0	1,48	+24.4
Tear index, $mN.m^2/g$ ± 0.18	3,58	4,38	+22.3	3,08	-16.2	2,93	-18.2	4,68	+30.7	4,88	+36.3
Opacity, % ±1.1	84,26	84,28	+0.02	84,48	+0.26	84,73	+0.6	84,00	-0.3	83,93	-0.39
Air resistance, s/100mL ±0.05	1,19	1,03	-13.4	0,78	-34.5	0,87	-26.9	1,28	+7.6	1,33	+11.8

***** The increment of strength properties after impregnation, with or without, UHP pre-treatment were calculated with respect to pulp ***E*** (Δ %).

It was found that PP impregnation, with 5% (w/v) concentration resulted on the significant decrease of handsheets strength properties, whereas with lower PP loadings (1% (w/v)) positive effects would be achieved upon PP impregnation. This last, would also be enhanced upon UHP treatment. The effect of UHP was insignificant when fibres were impregnated with 5% (w/v) PP solutions. The decrease on strength properties may be related with interference of PP precipitated particles on fibres surface, in considerable amount to hinder inter-fibres interaction, as the case of fillers in papermaking.[21]

In the case of samples impregnated with 1% (w/v) PP concentration, the opposite effect was registered, with and without UHP treatment. Strength properties such as tensile strength, burst and tear index, demonstrated significant improvements, which were even higher upon UHP treatment. It is possible that with small concentrations of PP, this compound conforms to fibre and hinder interfibre bonding.

Air resistance results for samples impregnated with 1% (w/v) concentration of PP rendered higher air resistance values, which are in agreement with a less porous and more organized/tightly packed fibres structure. On the other hand, high PP concentration originated the opposite results, which were explained by disordering PP effect of fibre bonding. The addition of salt like additive did not affect greatly pulp drainability, although in same cases a small decrease was found. As concerns the pulp's bulk, as expected, the addition of inorganic additives induced an increase of bulk.

The pulp impregnation with 1%PP (w/v) solution, under UHP, promoted not only fibres hydrophilicity, but also basic papermaking properties. Nevertheless, in terms of paper softness, it is noteworthy that PEG treated samples were softer to touch, than PP treated samples. Moreover, these last revealed to be problematic upon handsheets production due to its stickiness towards the handsheets dryer. Considering the benefits and the disadvantages of both PEG and PP additives, it was thought that the mixture of both could results on good hydration properties, together with less problems related to strength properties.

iii) Pulps doped with mixture of humectants

The effect on fibres impregnation with a PEG and PP mixture was also studied and the results achieved are presented in Table 7. 7.

Table 7. 7 - Physical and mechanical properties of pulp impregnated with and without impregnation with mixture of 0.5% (w/v) of PEG and 0.5%PP (w/v), with and without UHP treatment.

	E	EHP	Δ %*	Mixture	Δ %*	Mixture HP	Δ %*
ºSR ±0.9	17	16	-5.9	17	0	18	+5.9
Bulk, cm^3/g ± 0.10	2,030	2,077	+4.7	2,073	+2.1	2,046	+0.8
Burst index, $KPa.m^2/g$ ±0.08	1,03	1,10	+6.8	1,14	+10.7	1,37	+33.0
Tensile strength, N.m/g ±1.17	23,5	22,5	-4.3	24,3	+3.4	20,8	-11.5
Stretch, % ±0.06	1,19	0,93	-21.8	1,19	0	1,02	-14.3
Tear index, $mN.m^2/g$ ± 0.18	3,58	4,38	+22.3	4,72	+31.8	4,83	+34.9
Opacity, % ±1.1	84,26	84,28	+0.02	83,82	-0.5	83,86	-0.5
Air resistance, s/100mL ±0.05	1,19	1,03	-13.4	1,25	+5.0	1,27	+6.7

* The increment of strength properties after impregnation, with or without, UHP pre-treatment were calculated with respect to pulp **E** (**Δ %**).

The results revealed a small variation on strength properties, being the most conspicuous the shifts on tensile strength and stretch (%). It is possible that the use of both

additives in small dosage attenuated the negative effects previously seen, in higher loadings, individually, due to less interference with interfibre bonding.

It is noteworthy the increases found not only due the combination of PEG and PP, but also upon UHP treatments. These last were especially noticeable on burst and tear index, suggesting that fibres network were fortified by both additives, especially after UHP treatment (fibril disaggregation, increased accessibility and uniform dispersion of additives). The results on air resistance supported the aforementioned statements, as the increases were found in treatment assays, with and without UHP, unveiling a less porous and more efficiently packed fibres. In terms of opacity no significant changes were registered, which is indicative of a low interference of additives on papers opacity.

From the results achieved for all formulations, the samples that exhibited the best performance in terms of hydration skills and strength properties, were samples impregnated with 1%PP (w/v), followed by samples impregnated by the mixture of PEG and PP. Although the first yielded better results, its hand sheets exhibited higher roughness to touch, relatively to samples impregnated with mixture of humectants, which in terms of tissue paper production constitutes a rather relevant issue.

7.4. Conclusions

The positive effect of UHP on the impregnation of humectants in fibres was demonstrated. Overall, it was possible to observe higher sorption of these additives into fibres, upon UHP treatment. Besides, it was demonstrated that during UHP treatment of water soluble polymeric humectants (PEG), a discrimination effect on the sorption of oligomers of different molecular weight was observed. This fact affected strongly the retention of PEG on fibres.

Increased hydration skills were achieved for samples impregnated with humectants, which were further enhanced by UHP treatment. The use of humectants, such as PEG 400 and PP demonstrated the possibility of improving the hydration properties of fibres with increased moisture capture abilities and absorptivity by soaking in water. Additionally, it was found that even though these additives improved the hydration abilities of pulp, they also affect negatively strength properties, which required an optimization of the humectants formulation applied. These negative effects were assigned to interferences brought by additive on interactions between fibres that weakens their interfibre bonds.

Finally, by varying the additive loads it was possible to attenuate the abovementioned negative effects, on pulp strength properties, or even improving them. These variations were possibly related with a more controlled dispersion of additives, enough to avoid their interference with fibre bonding, while, at the same time, keeping high hydration properties.

It was also concluded that the formulation that enabled the best hydration/strength pulp properties was 1%PP (w/v), followed by mixture of both PP (0.5% (w/v)) and PEG (0.5% (w/v)), both subjected to UHP treatment.

7.5. References

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Chapter VIII

Effect of ultra-high pressure on the impregnation of additives

- Antimicrobial agents

Contents

8.1. Introduction

On nowadays modern society, antimicrobial finishing of materials has been gaining growing relevance. [1,2] Redefining tissue products to enhance hygiene is a way to minimize and contain the spreading of harmful microorganisms. An example of this would be Cascades® Antibacterial Towels. [3,4] In the case of natural fibres, such as cellulose, they exhibit a tendency to microorganism's growth, such as bacteria and fungi. These microorganisms are easily found almost everywhere and are able to multiply quickly when their basic needs are met, such as moisture, nutrients and temperature.[1,5]

The use of antimicrobial agents provides protection against pathogens and other microorganisms, which could origin either medical or hygienic problems. These antimicrobial agents differ in terms of chemical structure, effectiveness, method of application, its impact on humans and on the environment, as well as in its cost.[1,2]

To achieve the desired effect, an ideal antimicrobial agent should gather a few requirements, such as be effective against a broad spectrum of microorganisms, while displaying low toxicity to consumers. It should also be durable (be active for a long period of time) and compatible with the chemical and technological processes, in which it will be included. It also should be cost effective and not harmful to either the manufacturer or the environment. [5,6]

An example of an effective antimicrobial agent is polyhexamethylene biguanide (PHMB), which is a cationic polymer with cationic biguanide repeating units separated by hydrocarbon chain blocks of identical or dissimilar length. PHMB is a strong and broad spectrum antimicrobial agent with low toxicity, features that have attracted the attention for antimicrobial finishing in textile industry. This compound is frequently used as a disinfectant in the food industry and in the sanitization of swimming pools. It was also explored as a biocide in mouthwashes and wound dressings. [1,5,7,8]

In order to embody antimicrobial properties to cellulosic materials, these may be functionalized with antimicrobial materials either in bulk or by addition of encapsulated antimicrobial agents. This last strategy may result in improvements on the controlled delivery of these compounds and improve their activity. This method also aims to reduce the amount of antimicrobial agent applied (more efficient utilization) and to decrease negative effect of the final product, such as undesired variations of products properties (due to the interactions of the antimicrobial with the product matrix) or secondary effects to consumers (e.g. skin irritation), etc.[9–12]

Ultra-Hydrostatic high pressure, UHP emerges here, similarly to previous studies, as a prominent technique enhancing cellulosic fibres accessibility and thus facilitating chemicals implementation in fibres.[13–15] Accordingly, the main purpose of this work consisted in the impregnation of fibres with antimicrobial agent PHMB, with and without UHP treatment. The effects on UHP treatment on pulp impregnation with PHMB solution was evaluated in terms of antimicrobial properties of processed pulp and PHMB leaching in aqueous solutions. Additionally, the impregnation of cellulosic fibres, with and without UHP, with encapsulated PHMB was also investigated.

8.2 Materials and Methods

Similar to previous studies on the impregnation of additives, the raw material used was virgin hardwood pulp. As depicted before, this raw material was used as reference to avoid irregularities coming from the variability of recycled pulps lots. Thus, conventional industrial bleached *E. globulus* kraft pulp and an antimicrobial agent, (poly(hexamethylene biguanide) hydrochloride), PHMB (20% (w/w) solution, Arch UK Biocides), were kindly supplied by Renova FPA, SA. and used in the impregnation tests.

8.2.1 Impregnation of PHMB on cellulosic fibres

- P_2O_5, (98%, Acros Organics)

Different sets of samples, with and without UHP treatment, were impregnated with PHMB. The samples designations are presented in Table 8. 1.

Table 8. 1 – Samples designations.

Samples	Description
0.5%	Fibres impregnated with a 0.5% (w/v) solution of PHMB;
0.5% HP	Fibres impregnated with a 0.5% (w/v) solution of PHMB under UHP (500MPa, 10min);
0.1%	Fibres impregnated with a 0.1% (w/v) solution of PHMB;
0.1% HP	Fibres impregnated with a 0.1% (w/v) solution of PHMB under UHP (500MPa, 10min);
0.01%	Fibres impregnated with a 0.01% (w/v) solution of PHMB;
0.01% HP	Fibres impregnated with a 0.01% (w/v) solution of PHMB under UHP (500MPa, 10min);
0.001%	Fibres impregnated with a 0.001% (w/v) solution of PHMB;
0.001% HP	Fibres impregnated with a 0.001% (w/v) solution of PHMB under UHP (500MPa, 10min);
E	Standard pulp
E HP	Standard pulp subjected to UHP (500MPa, 10min)

For samples preparation, pulp was dispersed in PHMB solutions with different PHMB concentrations (0.5, 0.1, 0.01% and 0.001% (w/v)), resulting of 2% consistency pulp suspensions. For each PHMB load, two samples were prepared, one was subjected to UHP treatment (500 MPa, 10 min), while the other was subjected to agitation, under atmospheric pressure (reference). The UHP conditions were the same as suggested previously for the impregnation of other additives (500 MPa, 10 min). In the case of samples treated with UHP (0.5% HP, 0.1% HP, 0.01% HP and 0.001%HP), the pulp suspensions, with corresponding amount of PHMB, were placed into HDPE containers, sealed and then submitted to UHP (500 MPa, 10 min) on a Hyperbaric model 55 equipment. On the other hand, samples impregnated without UHP (0.5%, 0.1%, 0.01% and 0.001%), were left stirring for 10 min (the same time spent in the UHP treatment).

After the impregnation with PHMB solution, a part of the samples was filtered, air dried and then kept on a desiccator over P_2O_5 (0% relative humidity), while the other was employed in the preparation of standard handsheets. For comparative reasons, pulp samples without PHMB were also considered. Thus, pulp without any kind of treatment (without PHMB addition and without UHP treatment), was designated *Control*, and the pulp without addition of PHMB and subjected to UHP (2%, consistency, 500 MPa, 10 min), was designated as *Control HP*.

8.2.2 PHMB silica capsules.

- Ammonia solution (25 –28%, Sigma-Aldrich)
- Span® 85 (Sigma-Aldrich)
- Tween® 20 (Sigma-Aldrich),
- Tetraethyl orthosilicate (TEOS, 99.9%, Sigma-Aldrich)
- Cyclohexane 99.9% (Merck).

Silica capsules with PHMB were prepared according with a previously developed method [16], through reverse emulsion, using Span®85 and Tween®20 as surfactants, cyclohexane as co-solvent and an ammonia solution as catalyst. An oil phase was prepared by dissolving 1 g of Span®85 in 50 mL of cyclohexane. Afterwards, one drop of Tween®20 in 5 mL of PHMB solution, followed by the addition of 2.0 mL of ammonia solution (25–28%) (water phase), were added to the oil phase under stirring and a water-in-oil micro-emulsion was achieved. After a few minutes stirring, 2.0 mL of TEOS was added to the w/o micro-emulsion under vigorous stirring and kept in a closed vessel for 24 h. The precipitate was then filtered, washed with cyclohexane and dried at 60^{o}C.

To test capsules stability towards UHP treatment a diluted solutions of capsules (1 mL) was subjected to UHP (500 MPa, 10 min, on a hyperbaric model 55, Burgos, Spain, apparatus). The samples were analysed before and after the treatment by SEM analysis.

8.2.2.1 Impregnation with PHMB capsules

Pulp suspensions were impregnated with PHMB silica capsules. 2.5 g of pulp were dispersed in distilled water (2% consistency). After thoroughly dispersed, PHMB silica capsules were added making up a concentration of 0.1% (w/v) of capsules in solution. Two sets of samples were prepared, one destined for UHP treatment and another for impregnation solely by stirring. The first one was placed on a HDPE container, sealed and then subjected to UHP treatment (on a Hyperbaric model 55 equipment) during 10 min at

500 MPa, while the other was left stirring during the same time. Afterwards both samples were filtered, air dried and stored on a desiccator under P_2O_5.

8.2.3 Leaching tests

Leaching tests were performed (in duplicate) to investigate the release behaviour of PHMB from cellulosic fibres. 1 g of sample was weighted and placed into a beaker, already filled with 100 mL of distilled water, under stirring. Aliquots of solution were collected from time to time and analysed by UV-Vis spectroscopy.

8.2.3.1 PHMB quantification

The PHMB released during the leaching tests was monitored by UV-Vis spectroscopy, on an UV-vis spectrophotometer Evolution 220 (Thermo Scientific). Standard PHMB aqueous solutions were prepared (1, 2, 4, 5, 10, 20 mg/L), and its absorbance at 234 nm was measured, and used to derive a calibration curve correlating absorbance with PHMB concentration. The calibration curve is represented on Appendice F.

8.2.4 Handsheets preparation

Standard handsheets were prepared following ISO 5269-2:2004, on a Rapid-Köthen sheet former (Karl Schröder KG)

8.2.5 Physical and mechanical properties

Fibres drainability was evaluated by analysing the *Schopper-Riegler* degree according to ISO 5267-1:1999. Thickness, density and specific volume of prepared handsheets were evaluated according to ISO 534:2011. Tensile strength, stretch, tear index, burst index and air resistance (Gurley method), were evaluated following ISO 1924-2:2008, ISO 1974:2012, ISO 2758:2014, and ISO 5636-5:2013 norms, respectively. Opacity of handsheets were determined following ISO 2471:2008 using Elrepho tester (Lorentzen & Wettre).

8.2.6 Solid UV-vis reflectance

UV-vis diffuse reflectance (UV-vis DR, *k/s*) spectra were recorded on a UV-vis spectrophotometer Evolution 220 (Thermo Scientific) equipped by an ISA-220 reflectance accessory using $BaSO_4$ as background reference at scan velocity of 200 nm/min.

8.2.7 Scanning electron microscopy (SEM)

SEM (scanning electron microscopy) analysis of capsules was also performed in scanning electron microscope Hitachi S4100 at an accelerating voltage of 25 kV on carbon sputtered samples. For this analysis a diluted dispersion of capsules was prepared and deposited on a silica lamella, previously attached to a SEM support with carbon tape. Then samples were carbon sputtered, previously to SEM analysis.

In the case of handsheets of pulp impregnated with capsules, those were analysed in the same equipment at an accelerating voltage of 15 kV. In this case small pieces of sample were attached to a SEM support by carbon tape and then subjected to Au/Pd sputtering before SEM analysis.

8.2.8 Fourier transform infrared - FTIR

Fourier transform infrared (FTIR) spectra of the paper samples were collected using a spectrometer Bruker optics tensor 27 coupled to a horizontal attenuated total reflectance (ATR) cell, using 256 scans at a resolution of 4 cm^{-1}. The spectres were normalized according with 2900cm^{-1} band (C–H stretching vibration).

8.2.9 Antimicrobial analysis

- Gram-positive bacteria *Listeria innocua* (*L. innocua*, ATCC 33090), (Liofilchem)
- Gram-negative bacteria *Escherichia coli* (*E. coli*, ATCC 25922), (Oxoid)
- Rose Bengal Chloramphenicol Agar (RBCA) (Oxoid)
- 0.1% Peptone Salt Solution (Himedia)
- Tryptic Soy Agar (TSA) (Liofilchem)
- Plate count agar (PCA) (Liofilchem)
- Neutralizing solution:
    - Polisorbate 80 (Panreac)
    - Lecithin from egg yolk (VWR)
    - Histidine hydrochloride (Biochem)
    - Meat peptone (Liofilchem)
    - Sodium chloride (99%, Panreac)
    - Monobasic potassium phosphate (99%, Acros Organics)
    - Disodium phosphate dehydrate (99%, Chemlab)

The antimicrobial activity was assessed by a quantitative test towards a gram-negative bacteria *Escherichia coli* (ATCC 25922) and a gram-positive bacteria *Listeria*

innocua (ATCC 33090). The quantitative analyses were performed based on the methodology present in the NP EN ISO 20743:2007 norm, being used the *transfer method*. It consists on an evaluation method in which the test bacteria are placed on an agar plate and transferred onto paper samples of 38 mm diameter. The target microorganisms used in these trials were: *Escherichia coli* (ATCC 25922) and *Listeria innocua* (ATCC 33090). For each sample analysis with possible antimicrobial activity was carried another one, to the respective control sample (without UHP treatment and/or without PHMB). All samples were analysed in triplicate. In order to transfer the microorganisms to the target paper samples, 1.0 mL of a suspension at $1x10^6$ – $3x10^6$ CFU/ml was spread on the surface of a TSA plate (the excess was removed), and then samples were set forth the inoculum over 1 min. After that period, one sample (in triplicate) was microbiologically evaluated (0 hours of incubation) while another one, in triplicate, was closed in petri plates (without any agar) and remained 24 h at 37 ºC being analysed.

The microbiological analyses of the sample consisted in the paper sample washing inside a *stomacher* bag with a neutralizing solution over 2 minutes using a Stomacher 80 (Seward), and a consequently series decimal dilution of the resulting washing residue (with 0.1% Peptone Salt Solution) was performed, being plated 1.0 mL on PCA for *E. coli* and *L. innocua*. Afterwards, the plates were incubated at 37 ± 1 ºC for *L. innocua* and *E. coli*, 36 - 48 hours and 24 h respectively.

In all cases, Petri dishes containing 30–300 colony forming units (CFU) were selected for counting and the value of Log CFU for each paper sample was calculated with Equation 8.1, where C_B is the microbial load concentration per mL (CFU/mL), Z is the mean value of CFU/mL in the triplicated microbiological analysis and R is the dilution factor used for the bacterial enumeration; and Equation 8.2 where M is the bacterial number per test piece and V the volume of the neutralizing solution added in the washing process.

$$C_b = Z \times R \qquad \text{Equation 8. 1}$$

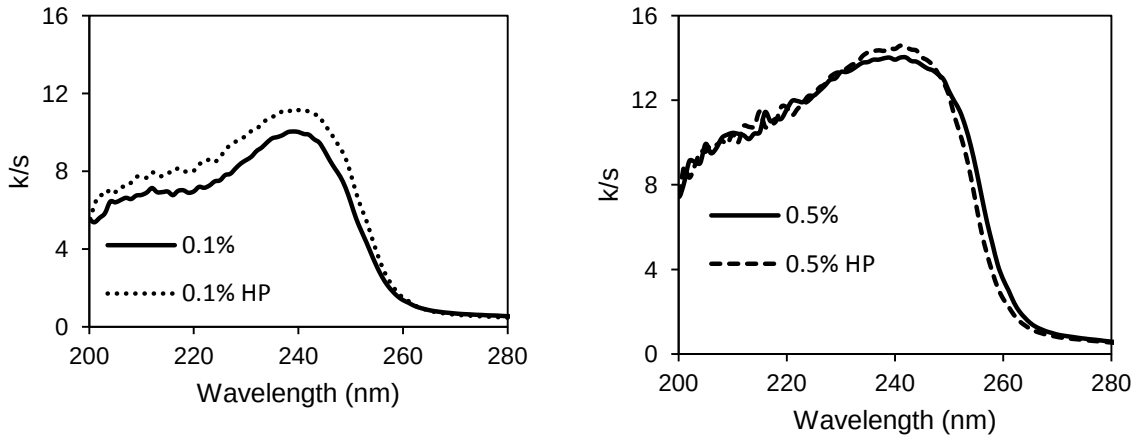
$$M = C_B \times V \qquad \text{Equation 8. 2}$$

8.3 Results and Discussion

8.3.1 Impregnation of PHMB

As in previous studies of impregnation with other additives, conventional industrial bleached *E. globulus* pulp, was impregnated with 0.1 and 0.5% (w/v) PHMB solutions, with and without UHP treatment. The samples designations were the same as presented in Table 8. 1.

The abovementioned samples were analysed by UV-Vis diffusive reflectance and their spectres are represented in Figure 8. 1. Looking into both sets of spectra it was possible to observe that samples subjected to UHP exhibited higher intensity at 234 nm (characteristic band of PHMB[17]) comparatively to untreated samples. Interestingly, in case of samples impregnated with 0.1% (w/v) solution this difference became even more noticeable, than after impregnation with 0.5% (w/v) solution. These results evidenced that samples, impregnated with UHP treatment exhibited a higher amount of PHMB, than pulp samples impregnated with PHMB solution without UHP. This fact was attributed to improved accessibility of fibres, upon UHP treatment that favoured PHMB adsorption on fibres. This improvement was particularly notable at low concentrations of PHMB in solution, when static sorption on fibre surface was not so significant.

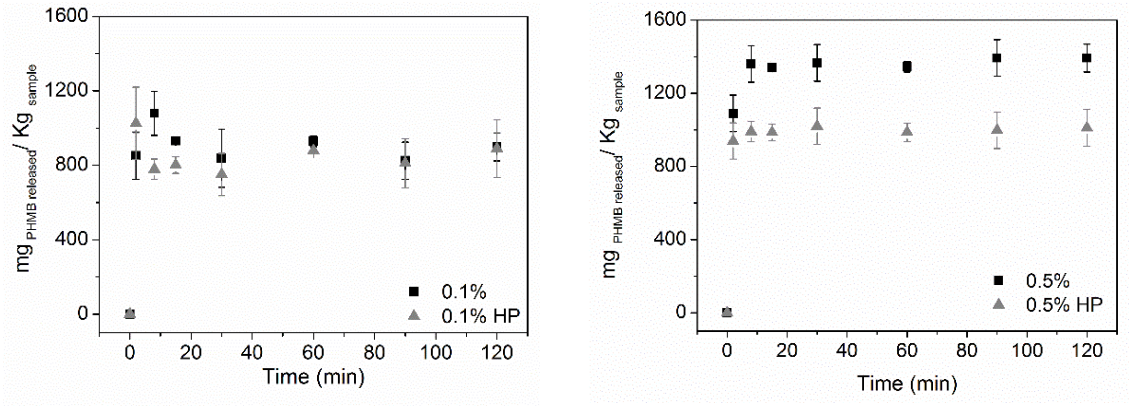


(a) (b)

Figure 8. 1 –UV-vis diffusive reflectance spectra of samples impregnated with 0.1 and 0.5% (w/v) PHMB solution with (0.1% HP and 0.5% HP) and without UHP (0.1% and 0.5%).

8.3.1.1 PHMB release studies

PHMB release in aqueous medium was also studied and the results achieved for the aforementioned samples are represented in Figure 8. 2.



(a) (b)

Figure 8. 2 – PHMB release profiles, in water, from samples impregnated with 0.1 (a) and 0.5%(w/v) PHMB solution (b), with (0.1% HP and 0.5% HP) and without UHP (0.1% and 0.5%).

The release profiles of PHMB revealed a decreasing of it removal, from samples subjected to UHP treatment, when compared to untreated samples. Additionally, this difference was even more evident for samples treated with a higher PHMB concentration (0.5% (w/v) PHMB solution).

These results diverge from the results achieved in the previous chapter (***Chapter 7***), where UHP induced higher uptake of humectants, accompanied by an accelerated additive release in water. It is proposed that positively charged PHMB interacts strongly with negatively charged cellulosic fibres. Additionally, due to improved fibres accessibility, upon UHP treatment, PHMB penetrates deep inside fibres structure favouring the formation of strong interactions with cellulose. These facts may contribute to the improved retention of PHMB. However, with increasing PHMB concentration in solution, the interactions by hydrogen bonds, between PHMB molecules, start playing an important role, leading to multilayer sorption on cellulosic fibres surface.[5,7,18] Therefore it is plausible that, for high PHMB loading, PHMB attached to fibres surface is bound to fibres by weak forces, and therefore its leaching becomes more easy in aqueous medium, when compared to fibres treated with low PHMB loads (predominance of ionic interactions).

8.3.1.2 Physico-mechanical properties

Considering the samples investigated so far, a set of samples was selected for further scrutiny, namely the ones treated with the low PHMB load (0.1% and 0.1% HP). Thus, handsheets of these were prepared and analysed for its physical and mechanical properties. The main purpose was to perceive how PHMB would interfere on the fibres properties and, at the same time, evaluate the effect of UHP treatment on the same properties. With this in mind the following samples were analysed: pulp without UHP treatment (***E***); pulp solely

treated by UHP treatment (***EHP***); pulp impregnated with PHMB without UHP treatment (0.1%); and pulp impregnated with PHMB and UHP treatment (0.1% HP). The results are presented in Table 8. 2. The data collected from both sets of samples, impregnated with PHMB, revealed significant losses in paper strength (tensile strength, burst and tear index) accompanied by slight gains on bulk and opacity. The losses in strength properties were more accentuated on samples impregnated with UHP treatment, than without UHP application.

It is known, from the literature, that PHMB (cationic polymer) interacts strongly with cellulose (negatively charged polymer) through ionic interactions and hydrogen bonds.[7] It is possible that by bounding with cellulose, PHMB interferes in fibres interactions (bonding), weakening the fibres network and therefore affecting paper's strength properties. This behaviour has been observed in paper for other additives of similar nature, such as debonding agents. These additives include cationic polymers (e.g. quaternary ammonium compounds) used to decrease fibre interbonding, and thus increase paper softness.[19–22] From this point of view it may be suggested that PHMB hinders interfibre bonding, conveying poor paper strength properties. Since UHP treatment promote PHMB sorption on fibres, the strength properties are particularly affected.

The decrease on air resistance of samples containing PHMB implies a material with higher porosity (more void space between fibres) and, therefore, less bonding area. Additionally, the small decrease found on ºSR further supports the reduction of interactions between fibres and, therefore, an easier water draining. Variation in bulk was expectable due to the diminished fibres bonding capacity.

Table 8. 2 – Properties of samples impregnated with PHMB (0.1% and 0.1% HP) and pulp without PHMB, with and without UHP (Control and Control HP).

Samples	E	E HP	Δ (%)*	0.1%	Δ (%)*	0.1% HP	Δ (%)*
ºSR, ±0.8	16,0	16,0	0	14	-12.5	14	-12.5
Bulk, cm^3/g, ±0.11	2.127	2.138	+0.5	2.207	+3.8	2.215	+4.1
Burst index, $KPa*m^2/g$ ±0.04	0.67	0.69	+3.0	0.52	-22.4	0.45	-32.8
Tensile strength, N.m/g, ±0.81	16.2	17.4	+7.4	14.2	-12.3	13.5	-16.7
Stretch (%), ±0.04	0.79	0.69	-12.7	0.73	-7.6	0.68	-13.9
Tear index, $mN.m^2/g$ ±0.11	2.03	2.51	+23,6	2.12	+4.4	1.84	-9.0
Opacity %, ±0.9	84.8	84.5	-0.4	85.6	+1.0	86.2	+1.6
Gurley's air resistance, s/100ml, ±0.05	0.74	0.79	+6.8	0.68	-8.1	0.64	-13.5

*All calculations were performed with respect to pulp ***E***.

Due to the loss of pulp strength properties, as a result of PHMB interference, it was interesting to study if decreasing PHMB load would attenuate such negative effects. To evaluate this possibility, new samples and handsheets were prepared with decreased PHMB loads (pulp treated with 0.01% (w/v) and 0.001% (w/v) PHMB solutions), with and without UHP treatment. The designations of samples were the same as presented in Table 8. 1.

Table 8. 3 – Properties of samples treated with PHMB 0.01% and 0.001%(w/v).

Samples	E	E HP	0.01%	Δ (%)*	0.01% HP	Δ (%)*	0.001%	Δ (%)*	0.001% HP	Δ (%)*
°SR, ±0.8	16	16	15	-6.3	16	0	16	0	16	0
Bulk, cm^3/g, ±0.11	2.127	2.138	2.197	+3.3	2.159	+6.8	2.168	+1.9	2.163	+1.7
Burst index, $KPa*m^2/g$ ±0.04	0.67	0.69	0.51	-23.0	0.57	-14.9	0.65	-3.0	0.53	-20.9
Tensile strength, N.m/g, ±0.81	16.2	17.4	12.7	-21.6	14.9	-8.02	17.0	+4.9	13.5	-16.7
Stretch (%), ±0.04	0.79	0.69	0.60	-12.7	0.79	0	0.84	+6.3	0.65	-17.7
Tear index, $mN.m^2/g$ ±0.11	2.03	2.51	2.43	+19.7	2.62	+29.1	2.72	+34.0	2.32	+14.3
Opacity %, ±0.9	84.8	84.5	86.1	+1.5	85.7	+1.1	85.1	+0.3	84.68	-0.17
Gurley's air resistance, s/100ml, ±0.05	0.74	0.79	0.70	-5.4	0.70	-5.4	0.77	+4.0	0.69	-6.8

*All calculations were performed with respect to pulp ***E***.

The obtained results are depicted in Table 8. 3. The pulp samples impregnated with diluted PHMB solutions (0.01% and 0.001% (w/v) PHMB solutions), revealed, in general, attenuated negative effects on their strength properties. This, however, was not the case of tear resistance, which increased. Since less molecules of PHMB are attached to fibres, less interference may be expected on the interfibre bonding. Thus, it is possible that the disruption of fibres network did not occur as easily as before, with relatively high concentration of PHMB in solution. This was mirrored by the small losses in strength properties of pulps with adsorbed PHMB (Table 8. 3). Moreover, it was also possible to observe an increase of tear resistance of pulps containing PHMB, especially for UHP processed pulp samples.

It was also not possible to conclude the role of UHP with different PHMB concentrations due to divergence in results between samples treated with 0.01% and 0.001% (w/v) PHMB solutions. With 0.01% (w/v) PHMB in solution, the negative effect imparted by antimicrobial agent was further attenuated, upon UHP treatment, whereas with 0.001% (w/v) PHMB solution the opposite trend was observed. This could be the result of a balance between the improved impregnation of PHMB by UHP and UHP effect on fibres (forced hydration, fibrils disaggregation, increased accessibility, etc.). Even though the

decrease on PHMB load attenuated the negative impact on strength properties, it may affect papers antimicrobial features. Hence, it was necessary to evaluate and confirm samples antimicrobial activity.

8.3.1.3 Antimicrobial activity

The antimicrobial ability of samples treated with different loadings of PHMB, was evaluated. The effect of the UHP treatment (500 MPa, 10 min) was also considered. Samples ***E*** (*control*) and ***EHP*** (*control HP*) were used as the control samples, thus taking into consideration not only the pulp itself, but also the effect of UHP on pulp. The tests were performed both on gram-positive and gram positive bacteria.

The method followed to analyse the antimicrobial activity of the above samples was based on the NP EN ISO 20743 norm, considering the following microorganisms:

- *Escherichia coli* ATCC 25922
- *Listeria innocua* ATCC 33090

This method is based on the transfer of microorganisms into the samples, through contact between the inoculum and the sample. This method is widely used to evaluate the antimicrobial activity in textile products, fibres, yarn, among others.

The first tests were carried out with *E. coli*, and the results obtained are displayed in Figure 8. 3.

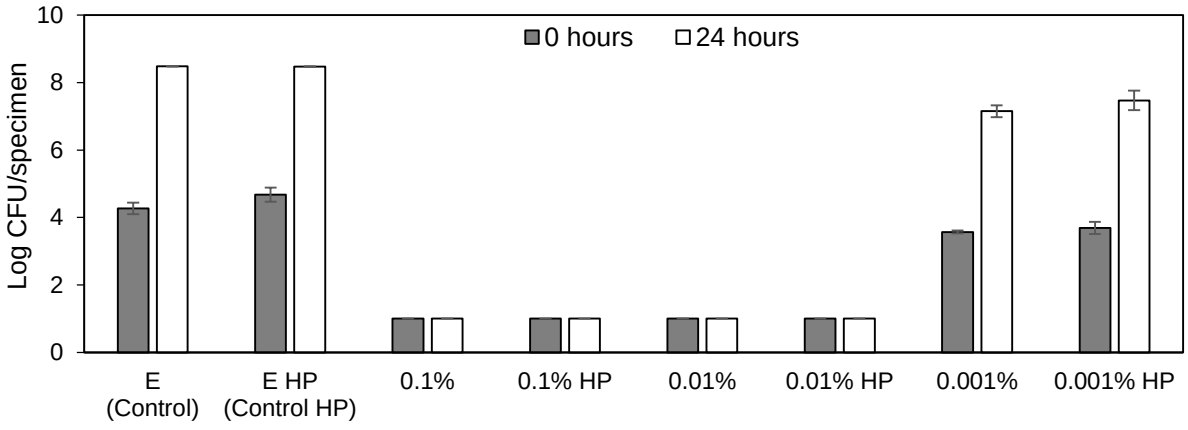


Figure 8. 3 – Results from the evaluation on the antimicrobial activity on samples subjected to the microorganism *E. coli.*

As expected it was noticeable that *control* samples did not hold any antimicrobial activity, as confirmed by the increase of Log CFU/specimen from 4.27±0.17 to 8.48±0.01, after a 24-hour incubation period. A similar behaviour was also observed for *control HP* sample in the same range of values.

Samples treated with high PHMB concentrations (0.1% e 0.01% (w/v)), with and without UHP treatment, clearly exhibited antimicrobial activity. This was quite evident by the values ≤1.00 Log CFU/specimen, already on zero time. Moreover, the same samples did not exhibited growth during incubation. As regards the samples treated with the lowest PHMB concentration (0.001% (w/v)), the observed behaviour was different. A notable microbial growth was observed during the incubation period from 3.57±0.04 to 7.15±0.18 Log CFU/ specimen and from 3.69±0.18 to 7.47±0.29 Log CFU/ specimen, for the samples impregnated without UHP treatment, and for the sample subjected to UHP treatment in PHMB solution, respectively.

The same analysis was performed with microorganism *Listeria innocua* and the results obtained are presented in Figure 8. 4.

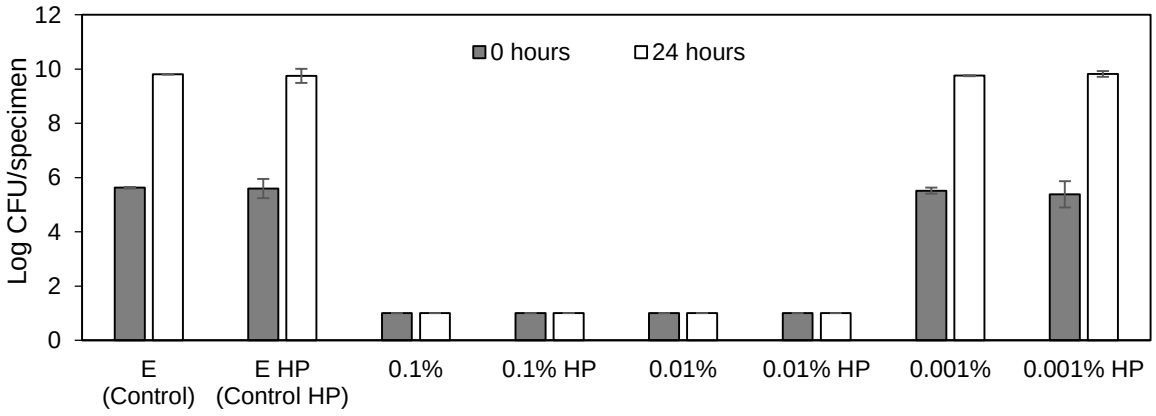


Figure 8. 4 - Results from the evaluation on the antimicrobial activity on samples subjected to the microorganism *L. innocua.*

The results with *L. innocua* were quite similar to those obtained with *E.coli. control* and *control HP* samples displayed an increase from 5.63±0.03 to 9.81±0.01 Log CFU/specimen, and from 5.59±0.35 to 9.75±0.26 Log CFU/specimen, respectively. It was demonstrated that samples treated with more concentrated PHMB solutions (0.1% and 0.01% (w/v), with and without UHP), on time zero, already exhibited values of ≤1.00 Log CFU/specimen. Microorganisms growth during the incubation period was not observed. Only for samples treated with lower PHMB concentrations (0.001% (w/v)), the microorganism's growth was observed during the incubation time from 5.51±0.11 to 9.75±0.02 Log CFU/specimen on the sample without UHP treatment, and from 5.39±0.48 to 9.82±0.10 Log CFU/specimen, for UHP treated samples.

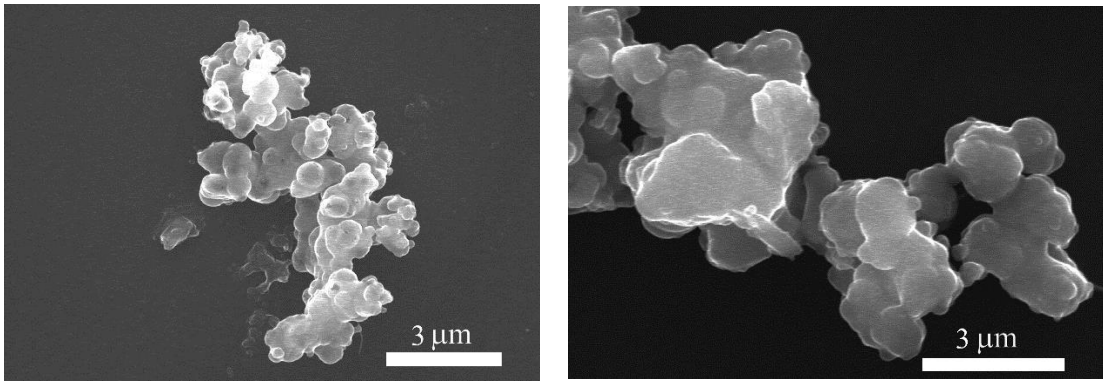
The differences observed between PHMB concentrations, as regards the antimicrobial activity on paper samples, is mainly related with the higher amount of PHMB required to avoid the growth of microorganisms. The PHMB in paper samples

treated with low PHMB concentrations may not be in range of the minimum required PHMB load to convey antimicrobial action. Therefore, for future applications, as regards both gram-positive and gram-negative bacteria, pulp treatment with both 0.1% and 0.01% (w/v) of PHMB solution may be sufficient for paper to display clear antibacterial properties. Nevertheless, it seems that the PHMB concentration of 0.01% (w/v) is preferable because of the minimal effect on the physical properties of pulp (Table 8. 3).

8.3.2 Impregnation with silica capsules

The functionalization of cellulosic fibres was also performed with PHMB encapsulated in silica capsules. The main purpose of this tests were to testing the capsules ability to be attached to fibres along with its antimicrobial activity potential, with and without UHP treatment. The capsules used in these tests were prepared and characterized by collaborators and had the same features of those in the literature.[16] PHMB capsules had diameters ranging from 270 nm to 1 μm, with a thickness of approximately 45 nm and estimated PHMB content of ca. 24% (w/w). [16]

Before the impregnation tests, silica capsules with PHMB were tested against UHP (500 MPa, 10 min), to evaluate the particles ability to maintain its integrity and stability towards high pressure environment. SEM (scan electron microscopy) images were obtained before and after the UHP treatment (500 MPa, 10 min) (Figure 8. 5). The SEM images revealed the integrity of capsules upon UHP treatment.

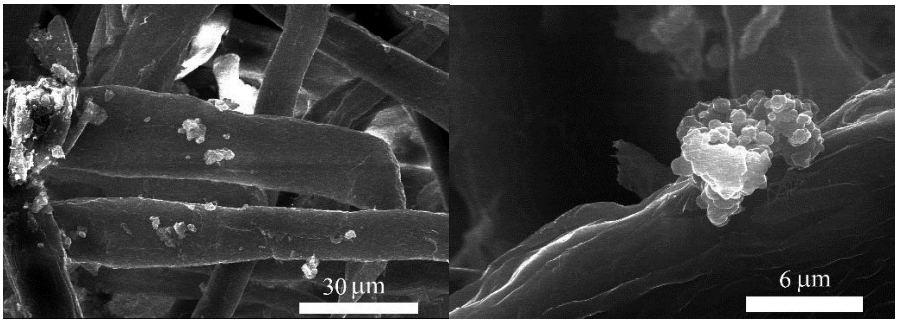


(a) (b)

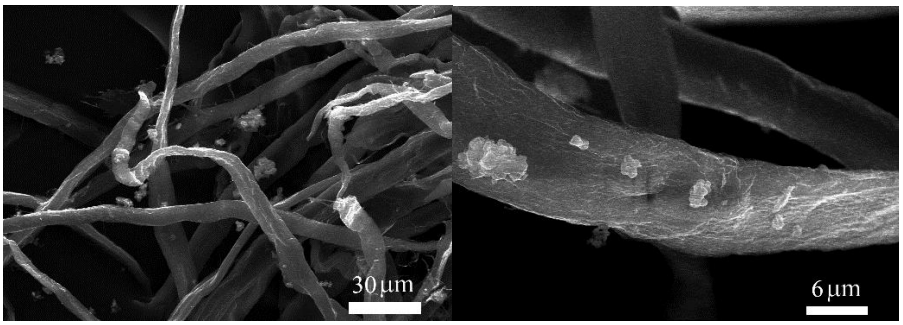
Figure 8. 5 – SEM imagens of PHMB silica capsules (a) and PHMB silica capsules submitted to HP (500 MPa, 10 min) (b).

The impregnation tests with capsules containing PHMB were carried out using the same cellulosic pulp and a capsules suspension of 0.1% (w/v). Two sets of samples were obtained, one impregnated with UHP (PHMB CPs HP) and another impregnated solely by stirring (PHMB CPs). To evaluate the deposition and distribution of capsules on cellulosic

fibres, SEM analysis was carried out (Figure 8. 6) The acquired images clearly showed the capsules in both PHMB CPs and PHMB CPs HP samples. This observation is in agreement with a good interaction between cellulosic fibres and PHMB capsules, possibly due to capsules positive charge surface, suggested previously. [16]



(a)



(b)

Figure 8. 6 –SEM images of cellulosic fibres impregnated with silica capsules, without UHP (a) and with UHP treatment (b).

The functionalization of fibres with PHMB capsules was also confirmed by FTIR (Figure 8. 7). The FTIR spectres revealed a substantial increase at 1028cm^{-1}, which was even more noticeable on the sample impregnated with UHP (PHMB CPs HP). This increase is related to the presence of PHMB silica capsules, namely to the vibrations of Si-O-Si stretching, from silica,[16] which prompted a significant increment on the a typical cellulose band attributed to the vibrations of C-O groups. The high intensity at 1028cm^{-1}, showed by the spectra of samples treated by UHP suggest the presence of a significant amount of silica capsules with PHMB. This increase in capsules capture is most likely related to the UHP ability to improve fibres accessibility and to facilitate the silica capsules adsorption on fibres.

Moreover, the aforementioned increases are also accompanied by an increase of intensity at 556cm^{-1}. It is suggested that this increase may be associated with vibration from oxygen atoms from both silica capsules and cellulose.[23,24]

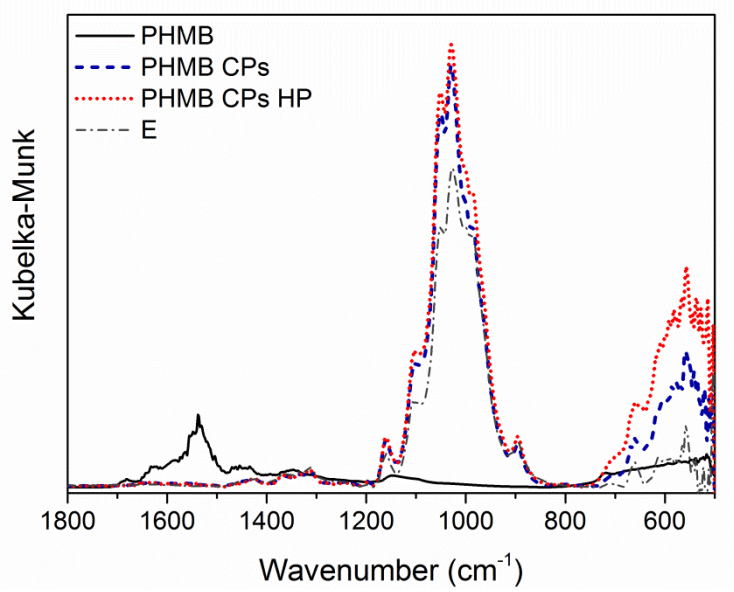


Figure 8. 7 – Normalized FTIR-ATR spectra of PHMB, PHMB CPs (fibres impregnated conventionally with capsules with PHMB), PHMB CPs HP (fibres impregnated with capsules with PHMB by UHP treatment) and ***E*** (hardwood pulp).

8.3.2.1 PHMB leaching

The release of PHMB from functionalized cellulosic fibres was also studied. Thus, the release tests were performed in water at room temperature (25±2ºC). The achieved release profiles are presented in Figure 8. 8. The curves revealed a similar release profile, for both samples, until 20min. After 20 min the release of PHMB was higher from samples treated by UHP. This was consistent with the opposite behaviour exhibited by samples impregnated with non-encapsulated PHMB (Figure 8. 2). A possible explanation for such phenomena could be related with the fact that PHMB doesn't interact with cellulose directly as in previous studies, due to its confinement in the silica capsules. This difference in scenario allows the diffusion of increased amounts of PHMB, during leaching into solution, because PHMB releases by controlled diffusion from capsules and is no longer hindered by its interaction with cellulose. Consequently, the higher amount of PHMB released by samples impregnated by UHP, indicates the presence of a higher amount of silica capsules attached to cellulosic fibres, as proposed by the FTIR results.

Normally cellulosic fibres exhibit a negative charge over a wide pH range, due to the presence of ionisable moieties such as carboxyl and hydroxyl groups, resulting from chemical processing, or from minor polysaccharides such as glucuronoxylans. Similarly, silica surfaces in contact with neutral aqueous solutions are also negatively charged. [25,26] However, the presence of PHMB (cationic polymer) in capsules (both encapsulated and on the shell pores) grants capsules a positively charged surface.[16] This fact favours the

capsules interaction with cellulose instead of being repealed due to the coulombic repulsion.

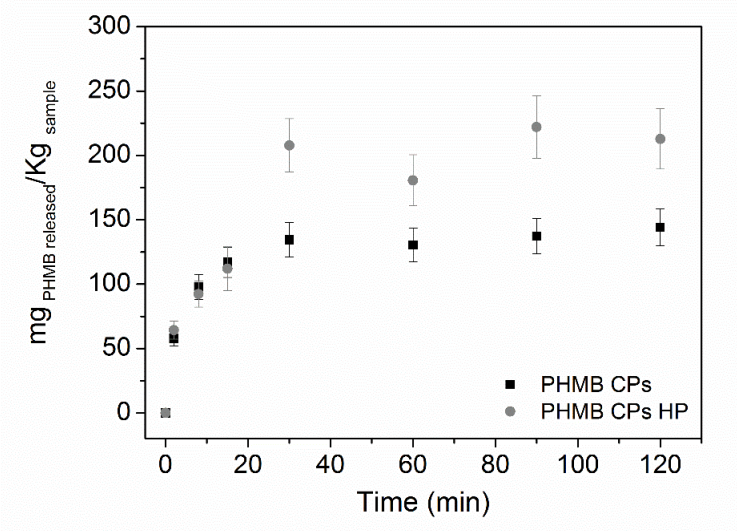


Figure 8. 8 – PHMB leaching profiles from PHMB CPs and PHMB CPs HP.

PHMB release from capsules sorbed on fibres was further monitored up to 24 h. The amount released from each sample was determined and presented in Table 8. 4. According to the results obtained it is possible to observe that, even after 24h, PHMB continues to be released from both samples. However, once more, PHMB CPs HP demonstrated superior release of PHMB than PHMB CPs (ca. +66%).

Table 8. 4 – Amount of PHMB released from PHMB CPs and PHMB CPs HP.

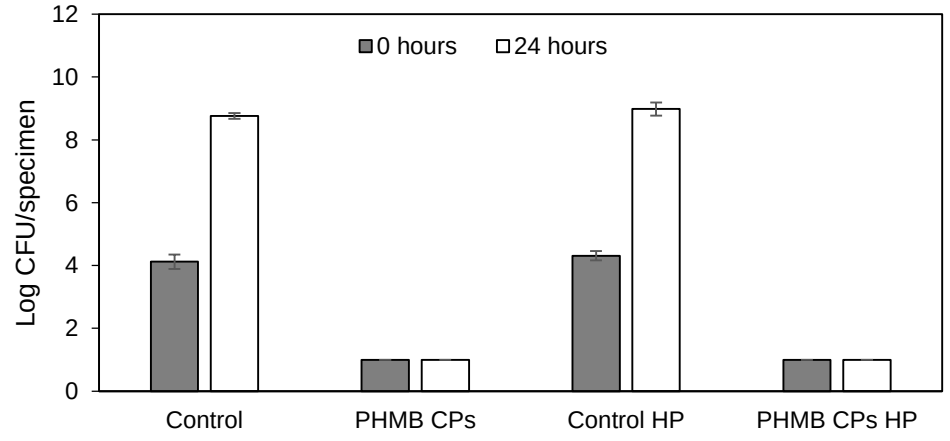
Sample	mg of PHMB released/Kg of sample	Increment (%)
PHMB CPs	179.9±9.0	+ 66.6
PHMB CPs HP	294.6±12.0	

The leaching assay with PHMB CPs and PHMB CPs HP samples were not complemented with mechanical and physical tests, with paper samples, due to insufficient materials for handsheets preparation. Namely, the reduced amount of capsules that was available for the study, which only permitted the preparation of a limited number of handsheets used for antimicrobial activity tests.

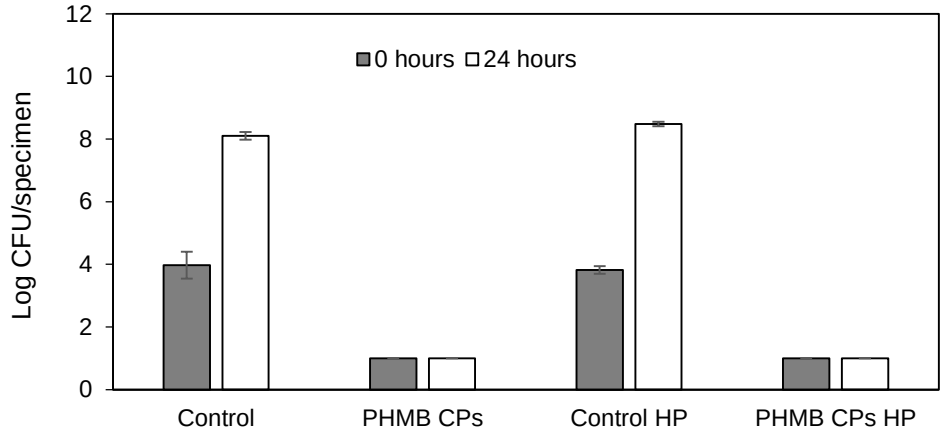
8.3.2.2 Antimicrobial activity

Fibres functionalized with PHMB silica capsules were also tested for antimicrobial activity. Handsheets were prepared from both pulp samples. Handsheets of *control* sample (pulp impregnated with empty silica capsules) and *control HP* sample (pulp impregnated with empty silica capsules and UHP treatment) were also prepared.

The antimicrobial tests were performed according to norm NP EN ISSO 20743:2009 with slight modifications, for the specimens *E. coli* and *L. innocua*. The results obtained are displayed above in Figures 8. 9a and 8.9b.



(a)



(b)

Figure 8. 9 - Evaluation of the antimicrobial activity on samples subjected to the microorganism *E. coli* (a) and *L. innocua* (b).

Using the microbiology tests it was possible to demonstrate the antimicrobial activity of both pulps doped with capsules, with two distinct microorganisms, after zero time and 24 h of incubation at 37 ºC.

These results suggest that both doped pulp samples, either with or without UHP treatment, possessed a minimal amount of PHMB necessary to inactivate microorganisms and thus inhibit its growth. It is possible that differences between the two doped pulps could be registered, if the PHMB amounts in the samples were lower than actually achieved, near the limiting load required to allow the antimicrobial activity.

8.4 Conclusions

The results achieved demonstrated once more that UHP enabled an improved impregnation not only of chemicals, but also of silica capsules. An improved impregnation of cationic antimicrobial polymer PHMB was demonstrated, thanks to UHP treatment. PHMB was more strongly attached to cellulosic fibres due to deeper penetration of PHMB and stronger interaction with cellulosic fibres. Although upon treatment with higher PHMB dosages, a frailer multilayer of PHMB, formed on the fibres surface would contribute to its easier leaching.

Nevertheless, even though UHP promoted positive results on PHMB impregnation, paper strength properties were negatively affected. These were posteriorly attenuated by reducing PHMB load in the impregnation assays, without affecting antimicrobial features. It is suggested that this negative effect of PHMB, on papers strength properties, could be reduced either by the use of encapsulated PHMB of by the addition of wet and dry strength agents (object for further studies).

The impregnation of microencapsulated PHMB was also demonstrated. It was seen that UHP treatment also enhanced the impregnation of capsules. It was suggested that the capsules positive charge, together with UHP enhanced accessibility, played a role enhancing capsules impregnation. Also, in opposite to the impregnation with PHMB alone, the results demonstrated that since PHMB is no longer interacting directly with cellulose, its release is controlled by its diffusion from capsules. Additionally, both samples impregnated with and without UHP demonstrated antimicrobial activity, which suggested that both systems provided PHMB in sufficient amount to inhibit microorganism’s activity.

8.5 References

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Chapter IX

Effect of ultra-high pressure on the impregnation of additives

- Perfumes

Contents

9.1. Introduction

The development of new consumer appealing products, such as tissue papers, has lead companies to research for different additives and methods to produce differentiated and unique products. [1–3] This was highlighted for the case of coloured papers (***Chapter 6***) and papers with antimicrobial properties (***Chapter 8***) and is also true for the case of papers with specific odour. Human's sense of smell identifies not only the quality of different odours, but also associates it, often unconsciously, with feelings ranging from agreeable to unpleasant associations. Relying on this many take advantage of it, since perfumed products become more attractive, while dreadful smells are used for the opposite effect. [4] Ergo, it is possible that by appealing to consumer sense of odour a positively impact on its buying behaviour may be verified. [1] Many companies have followed this strategy through the years, to enhance brand equity, by developing scent based trademark products.[5,6] An example of this would be Renova scented tissue papers.

To confer an appealing smell of freshly washed fabric or of perfume to a substrate, this last is commonly treated by spraying, coating or dipping, with a perfume or fragrance. However, the effects of the fragrance on substrates, wear of rapidly. [6]

As a way to retain longer perfumes on substrate, encapsulation has emerged as a potential method to enhanced odour durability on perfumed products.[6] Encapsulation confers protection to perfumes from surrounding adverse conditions (temperature, pH, water, etc), and thus enables a controlled and long perfume release.[7–9] Furthermore encapsulation also facilitates perfumes handling, which is an attractive point due to the irrigative nature of some fragrances. This approach of fragrances delivery improves its affinity towards the substrate, enables the reduction of the amount of perfume spent to embody odour on products (cost effective) and controls perfume release when necessary.[2,8–10]

9.2. Materials and Methods

Similar to previous studies on the impregnation of additives, conventional industrial bleached kraft pulp (***E***) was used as reference raw material. This pulp and fragrance Dovena new, DN, (Symrise, Inc.) were kindly provided by RENOVA-FPA, SA.

9.2.1. Synthesis of Dovena new silica capsules

- Hexadecyltrimethylammonium bromide (CTAB, 95%, Sigma-Aldrich)
- Ammonia solution (25 –28%, Sigma-Aldrich)
- Tetraethyl orthosilicate (TEOS, 99.9%, Sigma-Aldrich)
- Cyclohexane 99.9% (Merck).

Silica capsules with Dovena new (Si DN), were prepared by oil in water emulsion, using CTAB as surfactants, cyclohexane as co-solvent and an ammonia solution as catalyst. An oil phase was prepared by dissolving 5 mL of Dovena new in 20 mL of cyclohexane. Afterwards the water phase was prepared by adding 100 mg of CTAB to 35 mL of water and 0.25 mL of NH_4OH. The oil phase was added to the water phase, under stirring and an oil-in-water micro-emulsion was achieved. Then 2.0 mL of TEOS was added to the o/w micro-emulsion under vigorous stirring and kept in a closed vessel for 24 h. The precipitate was then filtered, washed and dried at 60 ^{o}C. Some of these capsules were then subjected to calcination at 550 ^{o}C, with a heat integrate of 5 ^{o}C/min, to investigate the perfume load on capsules. Also empty silica capsules were produced by performing the same experimental method but instead of Dovena new aqueous solution, the same volume of cyclohexane was used.

9.2.2. Capsules characterization

9.2.2.1. SEM

Scanning electron microscopy (SEM) analysis of capsules was also performed in scanning electron microscope Hitachi S4100, at an accelerating voltage of 25 kV on carbon sputtered samples. For this analysis a diluted dispersion of capsules was prepared and deposited on a silica lamella, previously attached to a SEM support with carbon tape. Then, samples were carbon sputtered.

In the case of handsheets of pulp impregnated with capsules (section **9.2.3.1.**), those were analysed in the same equipment at an accelerating voltage of 15 kV. In this case small pieces of sample were attached to a SEM support by carbon tape and then subjected to Au/Pd sputtering before SEM analysis.

9.2.2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed on a Sataram Labsys system under air atmosphere, with a heating rate of 10 ºC/min in the temperature range of 20 –800 ºC.

9.2.2.3. Zeta potential

Zeta potential analysis was performed on a Malvern Zeta Sizer Nano Series apparatus, using disposable plastic cells on capsules diluted dispersions. Complementarily each solution pH was also measured using a pH Meter, model HI2020 - edge® multiparameter, from Hanna Instruments.

9.2.3. Samples preparation

9.2.3.1. Samples impregnated with DN

For samples preparation, pulp was dispersed in distilled water (2% consistency), then DN was added to adjust the load of 5% ($w_{perfume}/w_{pulp}$). Two sets of samples were prepared, one was subjected to UHP (500 MPa, 10 min), while the other was only subjected to stirring for the same time. The UHP conditions used had in consideration results achieved in previous chapters, as regards the determination of the most advantageous UHP conditions, upon the impregnation of other additives.

Samples treated with UHP were placed into HDPE containers, vacuum sealed and were then submitted to UHP treatment (500 MPa, 10 min) on a Hyperbaric model 55 equipment. On the other hand, samples impregnated without UHP were left stirring for 10 min (the same amount of time spent on the UHP treatment). After the impregnation samples were used to prepare standard handsheets according with norm ISO 5269-2.

9.2.3.2. Samples impregnated with Si DN

To prepare samples impregnated with capsules, pulp was dispersed in distilled water (2% consistency), then Si DN were added making up a load of 5% (w_{SiDN}/w_{pulp}). Two replicas were prepared, one was subjected to UHP (500 MPa, 10 min), while another was subjected to agitation only, for the same time. Samples treated with UHP were placed into HDPE containers, sealed and then submitted to UHP (500 MPa, 10 min) on a Hyperbaric model 55, Burgos, Spain, equipment. On the other hand, samples impregnated without UHP were left stirring for 10min. Afterwards samples were used to prepare standard handsheets according with norm ISO 5269-2: 2004. These sheets were also analysed by SEM by placing a small cut of paper sheet on carbon tape already attached to a SEM

support. Then samples were carbon sputtered and analysed in the same equipment, previously mentioned, at 15 kV.

9.2.4. Fourier transform infrared - FTIR

Fourier transform infrared (FTIR) spectra of the paper samples were collected using a spectrometer from Perkin Elmer, model Spectrum BX coupled to a horizontal attenuated total reflectance (ATR) cell, using 256 scans at a resolution of 4 cm^{-1}. The spectres were normalized according with 2900 cm^{-1} band (C–H stretching vibration).

9.2.5. Total organic compounds (TOC) analysis

The amount of volatile organic compounds released by each samples was analysed on Laboratório da Qualidade do Ar Interior (IDMEC-Instituto de Engenharia Mecânica – FEUP, University of Porto). Thus, samples (handsheets) were reduced to smaller pieces, placed in impingers and subjected to N_2 purging, to drag volatile compounds into Tenax TA tubes for volatile organic compounds (VOCs) determination. The identification and quantification by a selective mass detector was performed using a chromatographer from Agilent Technologies model 6890N and a mass selective detector from the same brand, model 5973. All analyses were performed following norm ISO 16000-6. The analysis was preceded by thermal desorption from Tenax Tubes by means of a desorption system from DANI, model STD 33.50, coupled to the GC equipment.

9.3. Results and Discussion

The impregnation of cellulosic fibres with perfumes was performed following different approaches, one with perfume and the other with encapsulated perfume, with and without UHP treatment. Prior to any impregnation the capsules used for the impregnation of cellulosic fibres were characterized. It is noteworthy that the capsules employed on fibres impregnation were prepared, characterized and provided by collaborators, which work is still pending for publication.

9.3.1. Capsules characterization

9.3.1.1. Silica capsules with Dovena New (Si DN)

The provided capsules were analysed by SEM to evaluate its morphology. The acquired images are presented in Figure 9. 1. Although a population of capsules is observed, in these images it is still possible to observe a high amount of unpolymerized TEOS.

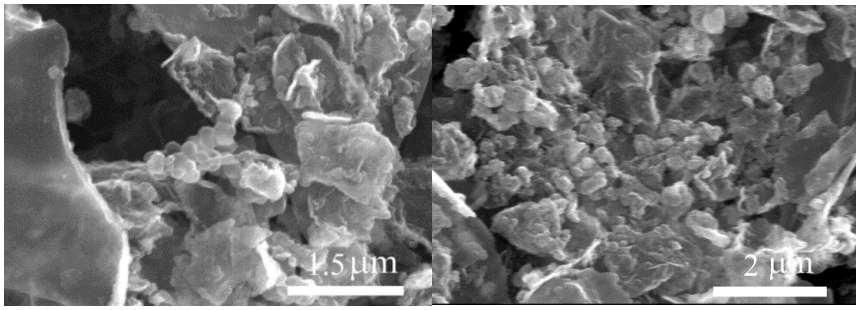

Figure 9. 1 – SEM images of Si DN.

Capsules thermal stability and its perfume content were also investigated by TGA analysis. The TGA analysis was performed on Si DN (silica capsules with Dovena new encapsulated), Si Calcined (calcined capsules) and on Si empty (empty capsules) (Figure 9. 2).

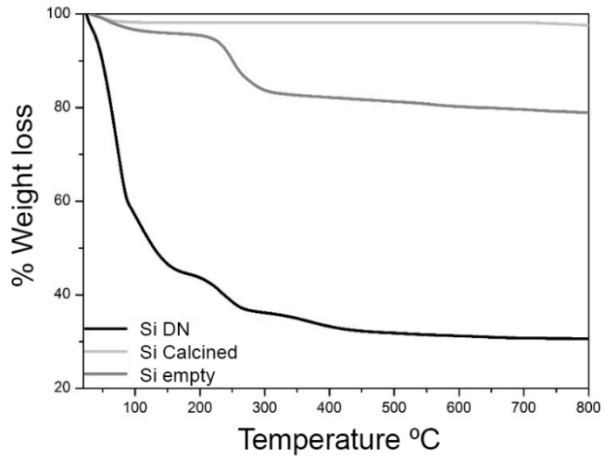

Figure 9. 2 –TGA thermogram from Si DN capsules, Si Calcined capsules and Si empty capsules.

Based on the TGA thermograms, it was possible to identify at ca. 100ºC a weight loss in each system (Si DN, Si calcined and Si empty) related with water molecules vaporization, along with volatile compound release, existing within the capsules. By comparing Si calcined with Si empty it was possible that the observed weight loss (ca. 19%) was mostly attributed to the degradation of TEOS, in the range of 225-275 ºC, that was not hydrolysed nor condensed during the synthesis reaction, along with the degradation of residual surfactants.

As concerns Si DN, the thermogram differs from Si empty, and the differences should be associated with the degradation of the fragrance compounds (complex mixture). The weight loss on the above mentioned temperature range is higher for Si DN reaching 67%. The difference in weight between Si empty and Si DN could be useful for the determination on the amount of fragrance encapsulated, which, in agreement with TGA, was of ca. 48% (w/w).

The Si DN capsules were also analysed for its zeta potential. The results revealed positively charged capsules, with a zeta potential of +36.2±1.9 mV (pH 6.1). This results suggests the presence of positively charged surfactant CTAB, on the capsules surface, even after capsules washing.

9.3.2. Fibres impregnated with Si DN

The fibres samples impregnated with silica capsules containing DN were analysed by SEM, to identify the presence of the capsules on the fibres. SEM images were achieved for both samples impregnated with and without UHP treatment. The images achieved are presented in Figure 9. 3. In both samples it was possible to identify the presence of the particles Si DN, meaning that adsorption on fibres succeeded, in both cases.

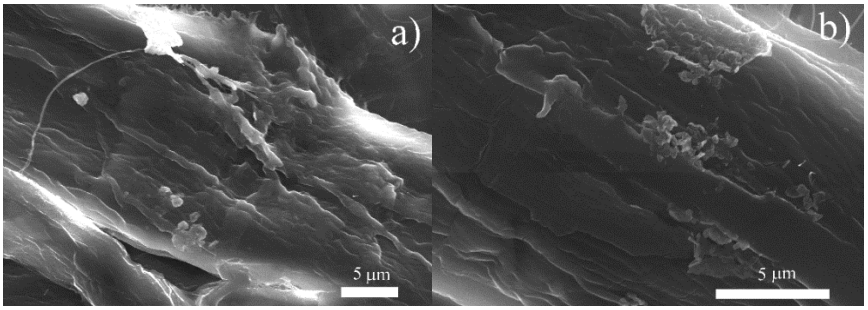

Figure 9. 3 – SEM images of the silica capsules in samples PHMB CPs (a) and PHMB CPs HP (b).

The presence of capsules on fibres was also monitored by FTIR (Figure 9. 4). The FTIR spectres of Si DN HP (fibres impregnated with capsules by UHP treatment) revealed a slightly higher intensity at 1023cm^{-1}, when compared with Si DN (fibres impregnated

with capsules without UHP treatment). This peak is related not only with the vibrations of C-O groups from cellulose, but also with the vibration of Si-O-Si stretching from silica. [11,12] Thus, it is possible that the slightly increased intensity of Si-O-Si band in sample Si DN HP may indicate the presence of higher content of silica capsules, comparatively to Si DN.

Additionally, at 557cm^{-1} samples impregnated with UHP treatment (Si DN HP), also revealed slightly higher intensities, when compared with samples impregnated without UHP treatment (Si DN). It is suggested that this may be associated with vibration from oxygen atoms from silica capsules.[11,12]

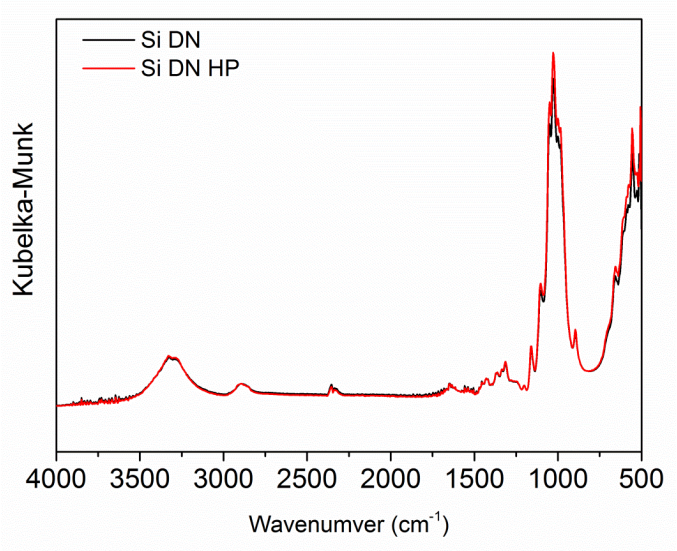

Figure 9. 4 - Normalized FTIR-ATR spectra of Si DN (fibres impregnated conventionally with capsules with Dovena new), Si DN HP (fibres impregnated with capsules with Dovena new by UHP treatment) and ***E*** (hardwood pulp).

9.3.2.1. Perfume release studies

Pulp samples impregnated with Si DN and perfume alone, with and without UHP treatment were evaluated for their retention of both capsules and the fragrance alone. The total volatile compounds were quantified by TOC analysis, on FEUP's air analysis Laboratory, following the ISO 16000-6 (2011) norm. To simplify, samples were designated as described in Table 9. 1.

Table 9. 1 – Samples designations.

Sample	Description
DN	Virgin fibres impregnated with fragrance by stirring for 10 min
DN HP	Virgin fibres impregnated with fragrance by UHP treatment (500 MPa, 10 min)
Si DNs	Virgin fibres impregnated with silica nanocapsules (with encapsulated fragrance), by stirring for 10 min
Si DN HP	Virgin fibres impregnated with silica nanocapsules (with encapsulated fragrance) with UHP treatment (500 MPa, 10 min)

The results achieved regarding the TOC analysis (total organic carbon) are presented in Table 9. 2.The results obtained revealed that, overall, pulp samples impregnated with DN or Si DN, by UHP treatment, demonstrated higher VOC (volatile organic compounds) release, relatively to those untreated by UHP. The higher release of VOCs (almost two times) on samples treated with UHP treatment was attributed to a higher sorption of perfume or encapsulated perfume (capsules) on cellulosic fibres. These results are in agreement with enhanced accessibility and diminished electrokinetic potential of fibres as discussed in previous chapters. Furthermore, in the case of encapsulated perfume in silica capsules, its positive charge may also exhibit affinity for negatively charged cellulosic fibres. Hence, it may be proposed, also, the improved affinity of fibres for silica particles, since more fragrance was released from fibres doped with capsules, after UHP treatment (Si DN HP), than without UHP treatment (Si DN).

Additionally, as expected, pulp functionalized with capsules released higher perfume content than pulp solely treated directly with perfume. Perfume volatile compounds escape rather easily from fibres. However, upon encapsulation, even though perfumes percentage correspond to half of capsules weight, the release is controlled being protected from surrounding severe conditions during handsheet preparation process and rendered high perfume release.

Table 9. 2 –VOCs release from samples impregnated with DN and encapsulated DN, with and without UHP.

	Concentration ($\mu g/m^3$)			
Compound	DN	DN HP	Si DN	Si DN HP
Butanol	9.08	13.3	n.d.	11.6
1-hexenol	n.d.	n.d.	n.d.	5.40
Limonene	0.81	n.d.	0.39	1.58
Decamethylcyclopentasiloxane	n.d.	n.d.	9.63	4.56
4-tert-buthylciclohexyl acetate	n.d.	n.d.	6.04	12.5
Diphenyl ether	n.d.	n.d.	0.21	0.38
α-cedrene	n.d.	n.d.	0.76	1.99
Thujopsene	n.d.	n.d.	1.26	2.83
VOCs	16.0	31.8	27.7	60.8

*n.d. = not detected

9.4. Conclusions

The impregnation of perfume and perfume containers on cellulosic fibres was performed with success, with and without UHP treatment. UHP aptitude to improve the efficacy of impregnation, not only of volatile compounds (perfume DN), but also of its encapsulated version was demonstrated. This allowed to demonstrate UHP potential towards other chemical systems such as VOCs and nanocarriers (capsules).

Additionally, the use of perfume capsules enabled a higher perfume retention and thus a higher release of this last with time, relatively to samples impregnated solely with perfume.

Moreover, the impregnation of cellulosic fibres, meant for tissue paper production, with encapsulated perfume, opens the possibility for products with high perfume content (more intense scent), without the usual excess of perfume (high spent on raw materials) required to maintain the scent intensity with time. Also, besides dosing and preventing the immediate release of all perfumes compound (controlled release), it is possible that it may also attenuate irritation reactions derived from skin direct contact with perfume compounds.

9.5. References

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Chapter X

Final remarks and future outlook

Contents

10.1.Final remarks and future outlook

The results achieved, permitted an improved comprehension of the phenomena behind ultra-high pressure (UHP) effect on the modification of cellulosic fibres.

Structural changes occurred under UHP treatment and were demonstrated for the first time on recycled fibres, and compared to virgin hardwood and softwood bleached fibres. It was demonstrated that the UHP induce forced hydration and rearrangements on cellulose fibrils. These rearrangements led to partial cocrystallization of conveniently oriented crystalline regions, resulting in it enlargement. Also, UHP treatment induced fibrils disaggregation, and thus enhanced cellulose accessibility. The enhancement of fibres accessibility was demonstrated by various techniques. In the case of recycled fibres, these results suggest a substantial reduction of hornification of fibres, which was demonstrated by the improved hydration abilities of recycled fibres.

It was demonstrated that UHP treatment also induces forced hydration and thus the formation of strongly bound water. Although identified its rigorous quantification was not possible. It was proposed that at least part of this strongly bound water is presented in the form of thermodynamically stable clathrate hydrates. As consequence, part of OH groups in cellulose became inaccessible. As future work it would be suggested a more advanced analysis over the quantification of strongly bound water on fibres, upon different UHP treatment conditions (time and pressure), and on the structure of formed clathrate hydrates.

The effect of UHP on the papermaking properties of fibres was also examined. The synergetic effect found, due to the combination of beating with UHP treatment, was especially witnessed for recycled fibres. Its capillary rise increased remarkably (more than double) and its refinability suggests up to 50% saving in energy. Besides the enhanced hydration skills of fibres, basic papermaking properties demonstrated either similar of improved values. Based on the strength and hydration properties gains and losses, for tissue paper production it is suggested that for recycled fibres the most indicated sequence was B1-HP-B2 (pre-beating stage, followed by UHP and by a last beating stage). Nevertheless, the best desired properties of papers will be dependent of pulp origin and the beating sequence applied under particularly optimized conditions. Due to the complexity of introducing a UHP equipment on a production line of tissue paper, further studies are suggested to evaluate its costs/benefits.

The structural changes induced by UHP was also demonstrated as a way to improve fibres accessibility towards different chemicals (dyes, humectants, antimicrobials and perfumes), enzymes and nanostructures. In the case of enzymes, it was found that the combination of enzymatic treatment with UHP led towards a significant improvement over

xylan removal, due to improved accessibility. It was also suggested that the enzymatic modification improved significantly the papermaking properties of recycled pulp. These improvements were related with the selective removal of xylan bound to impurities and to aggregated cellulose fibrils, on the fibre surface, thus favouring the ensuing swelling and inter-fibre bonding in paper. The pre-treatment of pulp with UHP and posterior enzymatic treatment revealed a synergetic effect on the mechanical properties of recycled pulp, which was attributed to the enhanced accessibility of fibres towards xylanase by forced hydration and favourable rearrangement of cellulosic fibrils in fibres after UHP pre-treatment. The increase of strength properties as result of UHP and xylanase treatment was up to 30%. However, in the case of recycled fibres, due to the reaction conditions (mildly acid media without surfactant), brightness was negatively affected, due to the re-precipitation of chromophore containing concomitants and loss of optical brightening agents. Therefore, new studies may be suggested, under different pH conditions to revaluate the effect of UHP and xylanase on recycled fibres brightness. It is also suggested studies to evaluate the combination of UHP treatment with other enzymes, to enhance recycled fibres quality (e.g. lipases).

The impregnation of dyes with UHP also demonstrated remarkable results, with enhanced impregnation of dye molecules and thus more intense colour shades. However, the equilibrium between the different agents during dyeing (dye, fixative and cellulose) was proved to be rather sensitive to UHP treatment, depending on the dye used. Therefore, it is suggested, either studies with a dye with known molecular structure and properties, or further insights and analysis upon the dyes used, namely, as regards their molecular structure, its affinity and substantivity towards cellulose, its interaction with fixative agents, etc.

The enhanced impregnation of additives by UHP treatment was also demonstrated with humectants. The use of UHP treatment not only improved impregnation, but it also resulted in the enhancement of cellulose hydrophilic character, which is a rather relevant aspect, in what concerns tissue papers. Although, fibres revealed improved hydration skills, losses in some papers strength properties were found. These losses were attenuated by decreasing humectants dosage, however, new studies are suggested to test other humectants and achieve an optimized formulation, in order to surpass the abovementioned negative effects. In another approach, it is also suggested, as future work, new tests considering the humectants used combined with dry- or wet-strength agents.

In another context the impregnation of the antimicrobial agent, cationic polymer PHMB (polyhexamethylene biguanide), with UHP revealed enhanced impregnation with

higher PHMB retention/fixation during leaching. This was attributed to a stronger and more effective impregnation of this compound due to UHP and PHMB cationic charge. Nevertheless, negative effects were produced on paper strength properties due to the disruptive action of PHMB. This was attenuated upon the decrease of PHMB dosage, without affecting the samples antimicrobial abilities, Nevertheless, new studies are suggested, with other antimicrobial agents, in order to confer paper antimicrobial properties, without affecting its strength properties. The conjugation with wet and/or dry strength additives is also suggested as future work.

Similarly to the previous case, silica encapsulated PHMB also revealed higher retention upon UHP, although a higher release of PHMB was verified. This opposite trend, relatively to the previous case, was attributed to PHMB not interacting directly with cellulose, turning its release diffusion dependent. Thus, the enhanced impregnation of capsules, due to UHP treatment, resulted in higher capsules retention together with higher PHMB release. Since, in these studies it was not possible to evaluate paper strength properties, due to limited access to PHMB capsules, it is suggested its evaluation, when capsules synthesis is optimized.

Similarly, to PHMB capsules, encapsulated perfumes (Dovena New), revealed higher impregnation upon UHP, confirming UHP ability to improve fibres accessibility, not only towards chemicals, but also towards different nanostructures. This was mirrored by a higher release of volatiles from samples impregnated with this nanomaterials, upon UHP.

Taking into consideration, not only the results achieved on the impregnation of additives with UHP treatment, but also the synergetic effect of beating with UHP treatment, further studies are proposed, as future work, to evaluate the effect of combining beating with UHP treatment, on the impregnation of additives in cellulosic fibres.

Appendices

A. GC-FID calibration curves

The quantification of neutral sugars was performed considering the calibration curve for each monosaccharide given on Figures A.1-6 where each monosaccharide mass is represented as function of the ratio of Peak area $_{Monosaccharide}$/Peak area $_{standard}$ (A/A(IS))

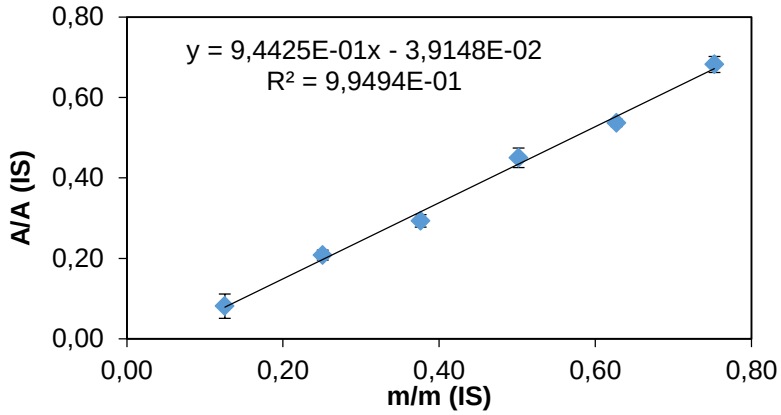

Figure A. 1 – Glucose calibration curve form neutral sugars quantifications.

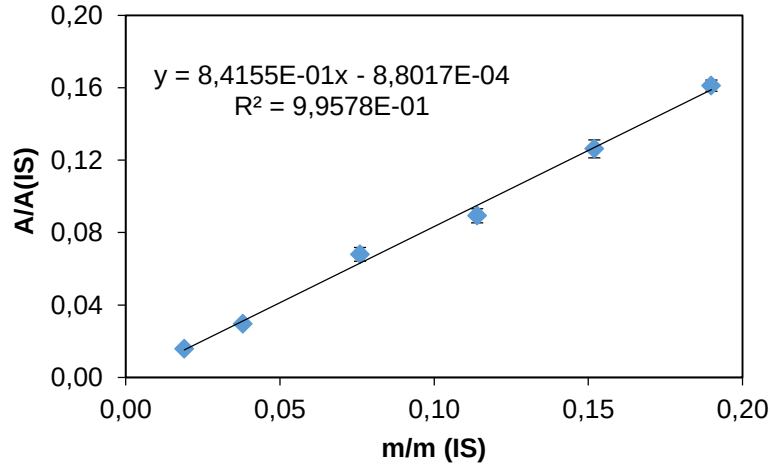

Figure A. 2 - Galactose calibration curve form neutral sugars quantifications.

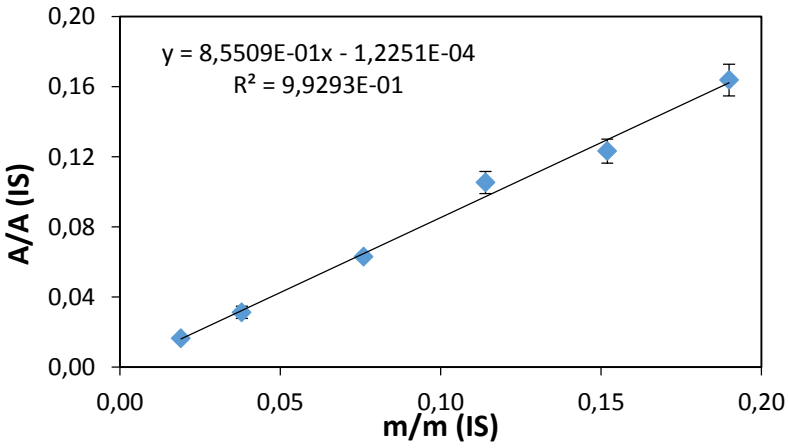

Figure A. 3 - Mannose calibration curve form neutral sugars quantifications.

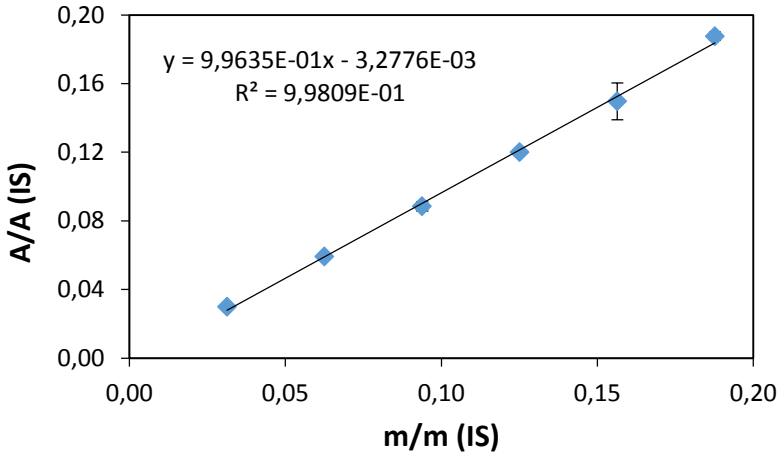

Figure A. 4 Xylose calibration curve form neutral sugars quantifications.

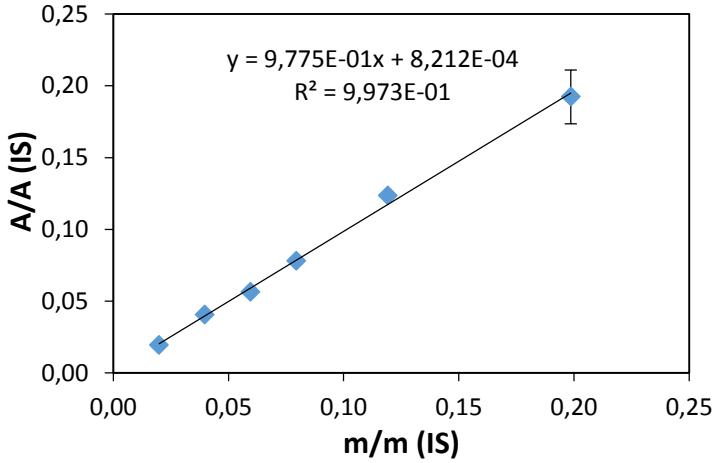

Figure A. 5 - Arabinose calibration curve form neutral sugars quantifications.

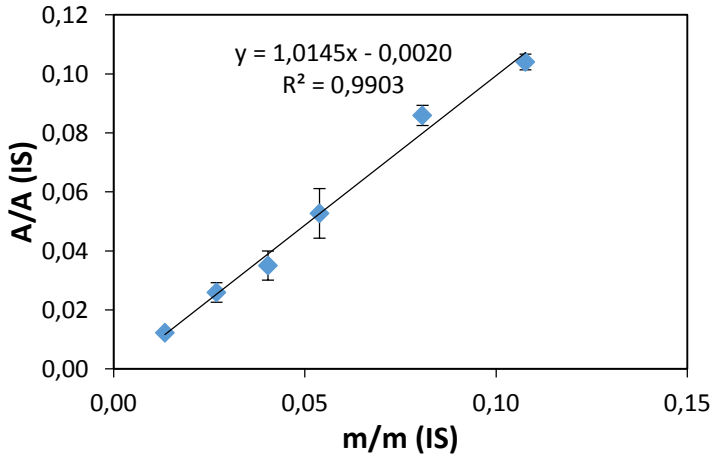

Figure A. 6 - Rhamnose calibration curve form neutral sugars quantifications.

B. ^{13}C NMR

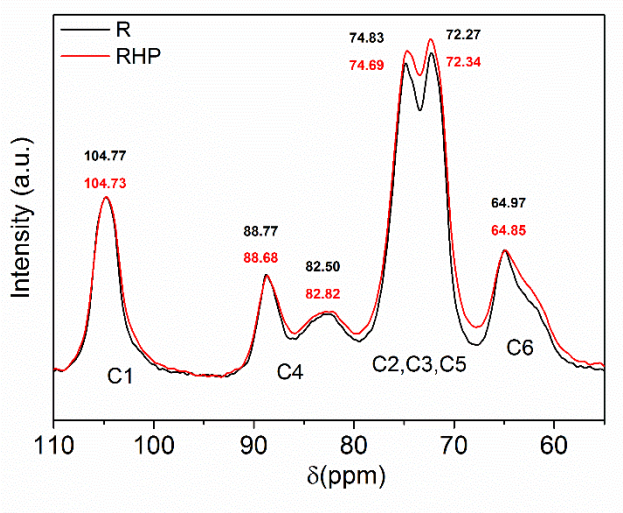

Figure B. 1 - ^{13}CNMR of ***R*** (recycled pulp) and ***RHP*** (recycled pulp treated with UHP, 400 MPa, 15 min).

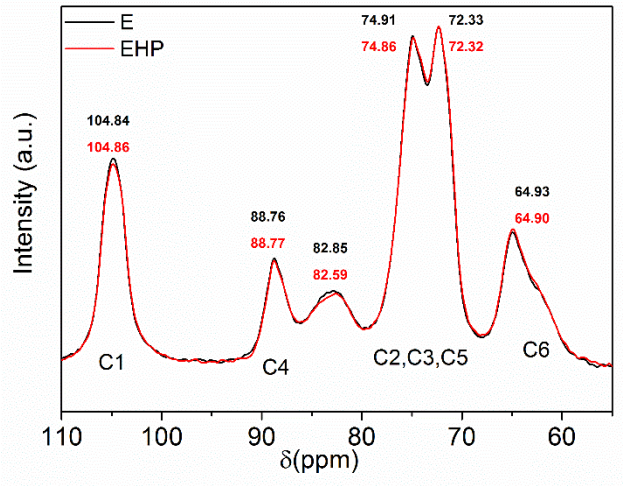

Figure B. 2 - ^{13}CNMR of ***E*** (hardwood pulp) and ***EHP*** (hardwood pulp treated with UHP, 400 MPa, 15 min).

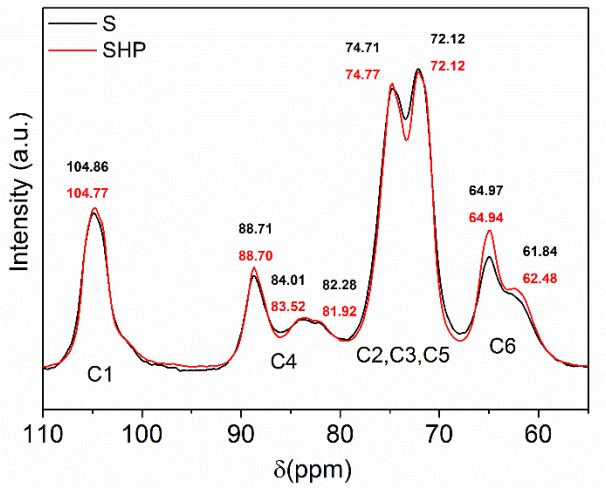

Figure B. 3 - ^{13}CNMR of ***S*** (softwood pulp) and ***SHP*** (softwood pulp treated with UHP, 400 MPa, 15 min).

C. DNS calibration curve

The determination of reducing sugars content was performed based on the calibration curve given in Figure B. 1.

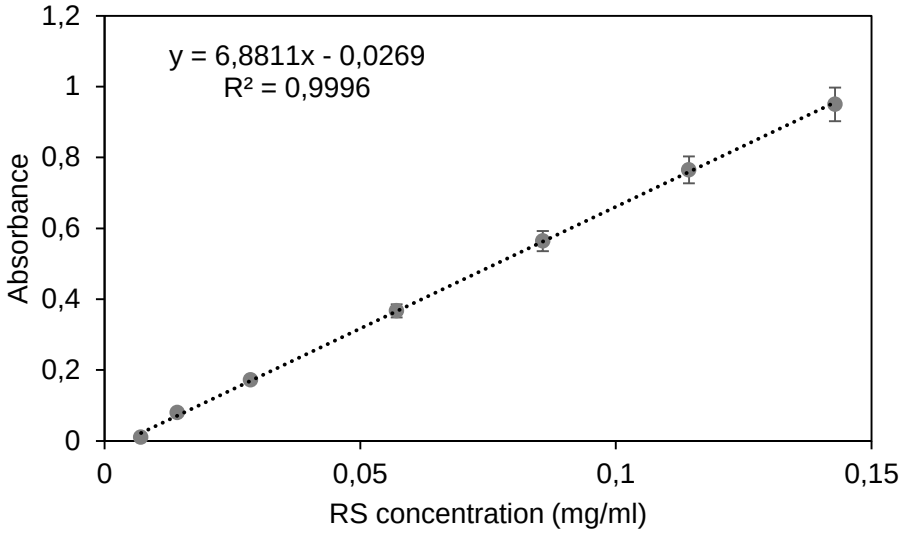

Figure C. 1 – DNS calibration curve with RS (glucose) concentration (mg/ml) as function of absorbance.

D. Bleedfastness results

Table D. 1- Pergasol Red 7BE bleedfastness results.

Pergasol Red 7BE	Bleedfastness degree			
	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% without UHP *	4	4	5	5
3% With HP *	4	4	5	5
3% with UHP (-5% Fixatives) *	4	4	5	5
3% with UHP (-10% Fixatives) *	4	4	5	5
3% with UHP (-15% Fixatives) *	4	4	5	5
4% without UHP*	4	4	5	5
Determination of FOL with UHP	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% (w_{dye}/w_{pulp}) Fixative load 1	4	5	4	5
3% (w_{dye}/w_{pulp}) Fixative load 2	4	5	4	5
3% (w_{dye}/w_{pulp}) Fixative load 3	4	4	4	5
3% (w_{dye}/w_{pulp}) Fixative load 4	4	4	4	5
3% (w_{dye}/w_{pulp}) Fixative load 5	5	4	4	5
3% (w_{dye}/w_{pulp}) Fixative load 6	4	4	4	5

*Samples impregnated considering the fixative optimum load (FOL) determined without UHP

Table D. 2 – Pergasol Black GNE bleedfastness results.

Pergasol Black GNE	Bleedfastness degree			
	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% without UHP*	4	4	4	5
3% With HP*	4	4	4	5
3% with UHP (-5% Fixatives)*	4	4	4	5
3% with UHP (-10% Fixatives)*	4	4	4	5
3% with UHP (-15% Fixatives)*	4	4	4	5
Determination of FOL with UHP	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% (w_{dye}/w_{pulp}) Fixative load 1	4	4	4	5
3% (w_{dye}/w_{pulp}) Fixative load 2	4	5	5	5
3% (w_{dye}/w_{pulp}) Fixative load 3	4	5	4	5
3% (w_{dye}/w_{pulp}) Fixative load 4	5	4	4	5
3% (w_{dye}/w_{pulp}) Fixative load 5	4	4	4	5
3% (w_{dye}/w_{pulp}) Fixative load 6	4	4	4	5

*Samples impregnated considering the fixative optimum load (FOL) determined without UHP

Table D. 3 – Cartasol Blue 3R-EU bleedfastness results.

Cartasol Blue 3R-EU	Bleedfastness degree			
	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% without UHP	5	4	4	5
3% With HP	4	4	4	5
3% with UHP (-5% Fixatives)	4	4	4	5
3% with UHP (-10% Fixatives)	4	4	4	5
3% with UHP (-15% Fixatives)	4	4	4	5
Determination of FOL with UHP	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% (wdye/wpulp) Fixative load 1	4	4	4	5
3% (wdye/wpulp) Fixative load 2	4	5	5	5
3% (wdye/wpulp) Fixative load 3	5	5	4	5
3% (wdye/wpulp) Fixative load 4	5	4	4	5
3% (wdye/wpulp) Fixative load 5	4	5	4	5
3% (wdye/wpulp) Fixative load 6	5	4	4	5

*Samples impregnated considering the fixative optimum load (FOL) determined without UHP

Table D. 4 – Pergasol Violet BN-TKZ bleedfastness results.

Pergasol Violet BN-TKZ	Bleedfastness degree			
	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% without UHP	4	4	4	5
3% With HP	4	4	4	5
3% with UHP (-5% Fixatives)	4	4	4	5
3% with UHP (-10% Fixatives)	4	4	4	5
3% with UHP (-15% Fixatives)	4	4	4	5
Determination of FOL with UHP	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% (wdye/wpulp) Fixative load 1	5	4	5	5
3% (wdye/wpulp) Fixative load 2	4	4	4	5
3% (wdye/wpulp) Fixative load 3	4	4	4	5
3% (wdye/wpulp) Fixative load 4	4	4	4	5
3% (wdye/wpulp) Fixative load 5	4	4	4	5
3% (wdye/wpulp) Fixative load 6	5	4	4	5

*Samples impregnated considering the fixative optimum load (FOL) determined without UHP

Table D. 5 – Pergasol Red 2G-Z bleedfastness results.

Pergasol Red 2G-Z	Bleedfastness degree			
	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% without UHP	4	4	4	5
3% With HP	4	4	4	5
3% with UHP (-5% Fixatives)	4	4	4	5
3% with UHP (-10% Fixatives)	4	4	4	5
3% with UHP (-15% Fixatives)	4	4	4	5
Determination of FOL with UHP	Distilled water	Acetic acid	Saliva Simulant	Olive oil
3% (wdye/wpulp) Fixative load 1	4	4	4	5
3% (wdye/wpulp) Fixative load 2	4	4	4	5
3% (wdye/wpulp) Fixative load 3	4	4	4	5
3% (wdye/wpulp) Fixative load 4	4	4	4	5
3% (wdye/wpulp) Fixative load 5	4	4	4	5
3% (wdye/wpulp) Fixative load 6	4	4	5	5

*Samples impregnated considering the fixative optimum load (FOL) determined without UHP

E. Humectants quantification – Calibration curves

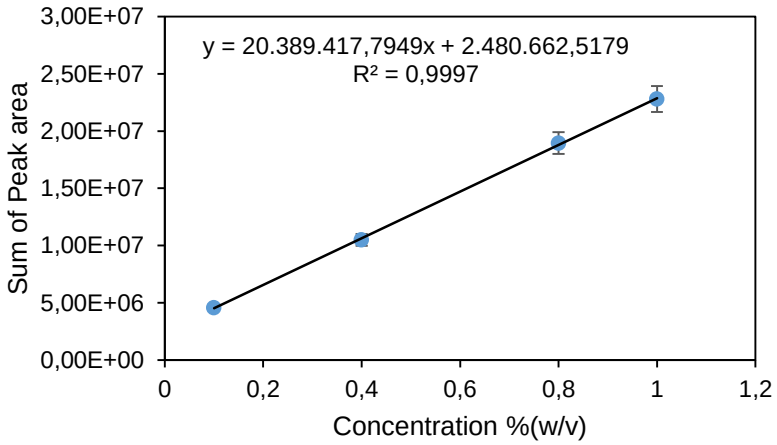

Figure E. 1 – Calibration curve for PEG 200.

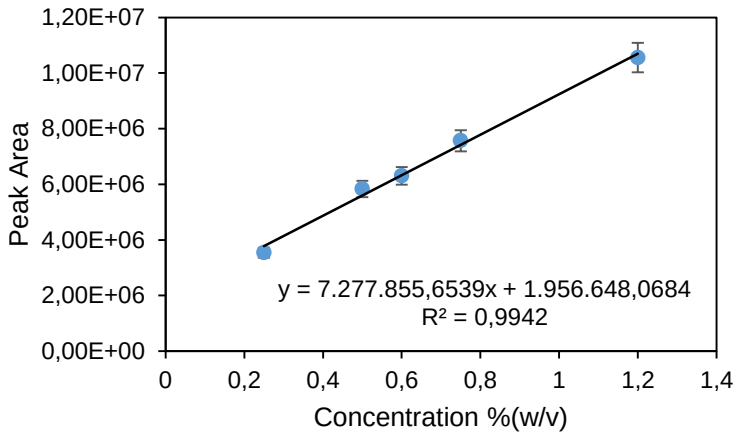

Figure E. 2 - Calibration curve for PEG 400.

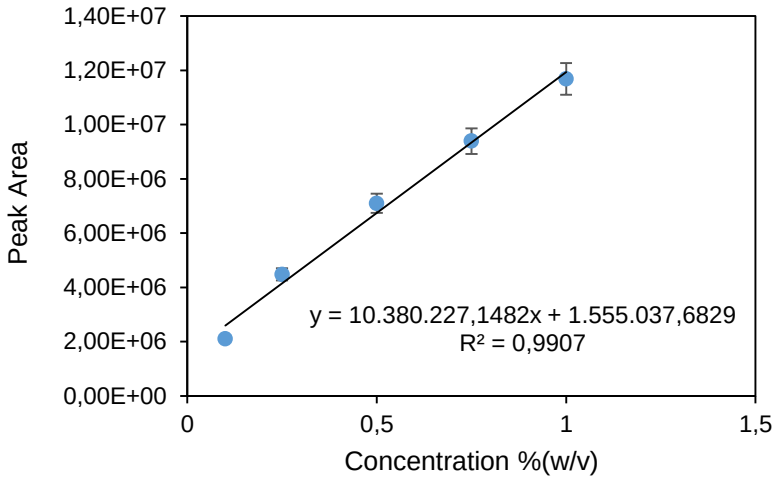

Figure E. 3 – Calibration curve for PEG 600.

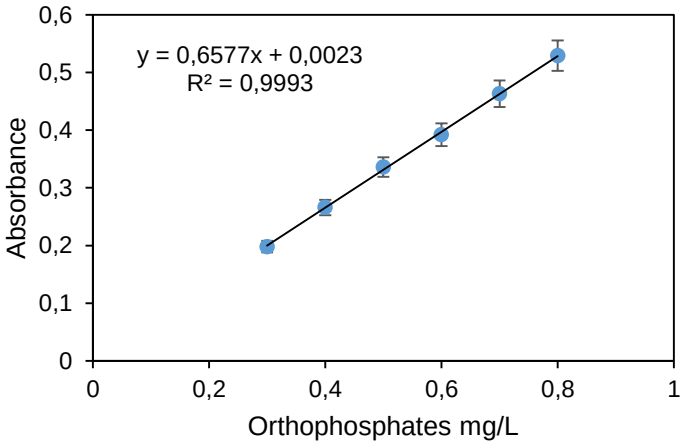

Figure E. 4 – Calibration curve for Orthophosphate quantification.

F. Antimicrobial quantification – Calibration curve

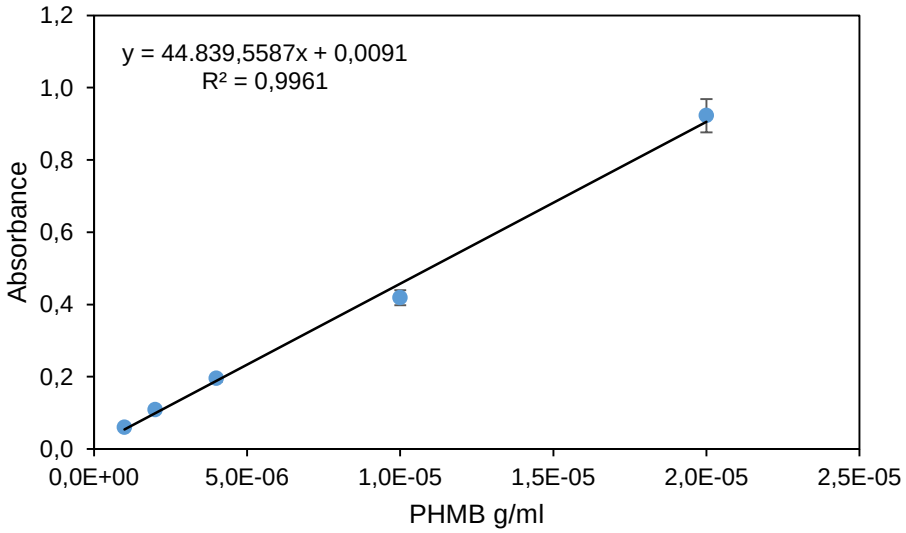

Figure F. 1 – PHMB calibration curve.