Universidade de Aveiro Departamento de Química
2017

Nuno Vasco Costa Gama Batista Melo

Functional bio-based polyurethane foams from industrial residues

Universidade de Aveiro Departamento de Química
2017

Nuno Vasco Costa Gama Batista Melo

Espumas de poliuretano funcionais derivadas de subprodutos industriais

Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Engenharia Química, realizada sob a orientação científica do Doutor Artur Jorge de Faria Ferreira, Diretor da Escola Superior de Tecnologia e Gestão de Águeda (ESTGA) da Universidade de Aveiro e da Doutora Ana Margarida Madeira Viegas de Barros Timmons, Professora Auxiliar do Departamento de Química da Universidade de Aveiro.

o júri

presidente

Professor Doutor Nelson Fernando Pacheco da Rocha
Professor Catedrático da Universidade de Aveiro

Professor Doutor João Carlos Moura Bordado
Professor Catedrático do Departamento de Engenharia Química, Instituto Superior Técnico, da Universidade de Lisboa

Professor Doutor Fernão Domingos Montenegro Baptista Malheiro de Magalhães
Professor Auxiliar do Departamento de Engenharia Química da Faculdade de Engenharia da Universidade do Porto

Professora Doutora Maria Helena Mendes Gil
Professora Catedrática Aposentada Convidade do Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra

Professor Doutor Dmitry Victorovitch Evtyugin
Professor Associado com Agregação do Departamento de Química da Universidade de Aveiro

Professor Doutor Artur Jorge de Faria Ferreira
Professor Coordenador da Escola Superior de Tecnologia e Gestão de Águeda, Universidade de Aveiro

Dedico este trabalho aos meus pais, aos meus sobrinhos, aos meus irmãos e aos meus avós.

agradecimentos

Em primeiro lugar agradeço aos meus orientadores, ao professor Doutor Artur Ferreira e à professora Doutora Ana Barros, pela orientação, esforço e disponibilidade que demonstraram ao logo de todo este percurso, pela ajuda, pelo apoio e acima de tudo pelas oportunidades concedidas.

Ao engenheiro Rui Silva, representande da SAPEC Química S.A., pela disponibilização de recursos para que esta tese fosse possivel e pela visão global das necessidades do mercado e indústria.

Ao colegas do departamento de Civil, a engenheira Claúdia Amaral e ao Doutor Tiago Silva pela ajuda essencial na elaboração dos modelos de simulação.

A todos co-autores dos diversos capítulos desta tese, à engenheira Belinda Soares, à Doutora Carmen Freire, ao professor Doutor Marco Costa, ao professor Doutor João Coutinho, ao engenheiro Farzin Mohseni, ao engenheiro Amin Davarpanah, ao professor Doutor Romeu Vicente, ao professor Doutor Vitor Amaral e ao professor Doutor António Carvalho, pelas suas colaborações imprescindíveis.

A todos os colegas de laboratório, em especial à Doutora Carla Vilela, e à engenheira Marina Matos pela ajuda, motivação, carinho e apoio.

Finalmente, o meu maior agradecimento é dírigido aos meus pais, irmãos e restante família pelo apoio incondicional, por quererem sempre o melhor para mim e por todo o incentivo que dão. Um beijinho muito especial para os meus sobrinhos.

Obrigado a todos.

palavras-chave glicerol não refinado, espumas de poliuretano, sustentabilidade.

resumo

Considerando a dependência da indústria de espumas de poliuretano (PUFs) de recursos fósseis, é necessário encontrar alternativas, substituindo os recursos derivados do petróleo, por recursos renováveis. Além disso, materiais funcionais ecológicos com maior valor acrescentado são cada vez mais necessários. A presente tese aborda estas necessidades explorando a utilização de glicerol não refinado (CG), um subproduto da indústria de biodiesel, como poliol na produção de PUFs.

Devido à variabilidade da composição química do CG, o efeito da sua composição nas propriedades das PUFs foi estudado, tendo-se verificado que os ácidos gordos e ésteres metílicos poderão atuar como tensoactivos, homogeneizando a estrutura celular das espumas, baixando assim a sua densidade e condutividade térmica. Seguidamente, foi estudado o efeito dos principais componentes das formulações usadas na produção de espumas sobre as respetivas propriedades utilizando o planeamento de experiências (DoE). Este estudo permitiu verificar que que a densidade e a condutividade térmica das espumas estão relacionadas com as quantidades de agente de expansão e tensoactivo, enquanto que as propriedades mecânicas dependem das quantidades de isocianato e de catalisador.

No sentido de preparar novos materiais funcionais e ecológicos com maior valor acrescentado, foram desenvolvidas formulações com o objetivo de melhorar o conforto térmico e a eficiência energética, reduzir a flamabilidade e melhorar o isolamento sonoro das PUFs. Através da adição de materiais de mudança de fase (PCMs) e grafite expansível (EG) não se conseguiu obter melhorias ao nível do conforto térmico das espumas, mas a adição de 5% de EG melhorou consideravelmente as suas propriedades de reação ao fogo. Verificou-se também que as espumas derivadas de CG apresentam boas propriedades de absorção sonora, podendo estas ser melhoradas para baixas frequências pela adição de outro poliol renovável derivado de borras de café.

Por fim, foi ainda desenvolvido um método de reciclagem de PUFs, em que o produto obtido foi utilizado com sucesso como substituinte parcial do CG na produção de espumas.

keywords Crude glycerol; polyurethane foams; sustainability.

abstract

In view of the dependence of the polyurethane foams (PUFs) industry on fossil resources, there is a need to find alternatives such as the replacement of petrol derived resources by those from renewable resources. Additionally eco-friendly functional materials with higher added value are ever more in demand. The present project, addresses these needs by exploring the use of crude glycerol (CG), a byproduct of biodiesel industry as the polyol component in the production of PUFs.

As the chemical composition of CG is variable, the effect of CG composition on PUFs properties was studied and it was observed that fatty acids and methyl esters can act as surfactants, improving the homogeneity of the cellular structure of the foams and subsequently decreasing their density and their thermal conductivity. Next, the effect of the main components used in PUFs formulations on their properties was studied using the design of experiments (DOE) tool. The results obtained confirmed that the density and thermal conductivity of the foams are related with the blowing agent and surfactant content, while the mechanical properties are associated with the isocyanate and catalyst content.

As regards the preparation of new functional and ecological materials with higher added value, formulations have been developed aiming at materials for enhanced thermal comfort and energy efficiency, improved reaction to fire and better sound insulation. The addition of phase change materials (PCMs) and expanded graphite (EG) did not bring improvements regarding the thermal comfort, but the addition of 5% of EG improved the reaction of the foams to fire significantly. Furthermore the CG derived foams presented good sound absorption properties, which can be improved for lower frequencies by the addition of another renewable polyol derived from the liquefaction of coffee grounds.

Finally, method for recycling of PUFs was developed and the product obtained was used as a partial substituent of GC in the production of foams.

List of publications

List of publications related and during the PhD period:

Papers

Nuno V Gama, Belinda Soares, Carmen SR Freire, Rui Silva, Artur Ferreira and Ana Barros-Timmons, *"Effect of unrefined crude glycerol composition on the properties of polyurethane foams*", Journal of Cellular Plastics, DOI: 10.1177/0021955X17732304

Nuno Gama, Rui Silva, António P.O. Carvalho, Artur Ferreira, Ana Barros-Timmons, *"Sound absorption properties of polyurethane foams derived from crude glycerol and liquefied coffee grounds polyol"*, Polymer Testing, 62,13-22 (2017)

Nuno Gama, Luis Cadillon Costa, Vitor Amaral, Artur Ferreira, Ana Barros-Timmons, *"Insights into the physical properties of biobased polyurethane/expanded graphite composite foams"*, Composites Science and Technology, 138, 24-31, (2017)

Nuno V. Gama, Rui Silva, Marco Costa, A. Barros-Timmons, A. Ferreira, *"Statistical evaluation of the effect of formulation on the properties of crude glycerol polyurethane foams"*, Polymer Testing, 56, 200-206, (2016)

Gama, N.V., Soares, B., Freire, C.S.R., Silva, R., Neto, C.P., Timmons, A.B., Ferreira, A., *"Bio-based polyurethane foams towards applications beyond thermal insulation*", Materials and Design, 76, 5, 77-85, (2015)

N. V. Gama, B. Soares, C. S. R. Freire, I. Brandão, R. Silva, C. Pascoal Neto, A. Barros-Timmons, A. Ferreira, *"Rigid polyurethane foams derived from cork liquefied at atmospheric pressure"*, Polymer International, 64, 2, 250-257, (2015)

B. Soares, **N. V. Gama,** C. S. R. Freire, I. Brandão, R. Silva, C. Pascoal Neto, A. Barros-Timmons, A. Ferreira, *"Spent coffee grounds as a renewable source for ecopolyols production"*, Journal of Chemical Technology and Biotechnology, 90, 8, 1480-1488, (2015)

Proceedings

N. V. Gama, A. Barros-Timmons, J. A. P. Coutinho, C. Amaral, T. Silva, R. Vicente, A. Ferreira, "*Enhancement of thermal properties of crude glycerol polyurethane foams*", Oral communication, AAMC 2016 – Miami, USA, 2016

N. V. Gama, B. Godinho, R. Silva, A. Barros-Timmons, A. Ferreira, "*Flame retardant properties of crude glycerol polyurethane foams filled with expanded graphite*", Oral communication, ICMTech 2016 – Delhi, India, 2016

N. V. Gama, R. Silva, C. S. R. Freire, C. Pascoal Neto, A. Barros-Timmons, A. Ferreira, "*Rigid polyurethane foams from unrefined crude glycerol – study of crude glycerol composition*", Oral communication, Mat´Cell 2015 – Aveiro, Portugal, 2015

N. V. Gama, R. Silva, C. Pascoal Neto, A. Barros-Timmons, A. Ferreira, "*Acoustic and sound absorption properties of crude glycerol and coffee grounds derived polyurethane foams*", Oral communication, AMWC 2015 – Stockholm, Sweden, 2015

Other communications

N. V. Gama, R. Silva, A. Barros-Timmons, A. Ferreira, "*Functional bio-based polyurethane foams from industrial residues*", Oral communication, MatCel'2017 & DynMatCel'2017 – Aveiro, Portugal, 2017

Bruno Godinho, Ricardo Santos, **Nuno Gama**, Rui Silva, Ana Barros-Timmons, Artur Ferreira, "*Purification of crude glycerol, by-product of biodiesel production*", Poster communication, Jornadas CICECO 2016 – Aveiro, Portugal, 2016

Bruno Godinho, Ricardo Santos, **Nuno Gama**, Rui Silva, Ana Barros-Timmons, Artur Ferreira, "*Desalinization of crude glycerol, by-product of biodiesel production*", Poster communication, ECO-BIO 2016 – Rotterdam, Netherlands, 2016

B. Godinho, R. Santos, **N. Gama**, R. Silva, A. Ferreira, "*Enzymatic synthesis of poly(glycerol sebacate) from crude glycerol*", Poster communication, RRB 2015 – York, United Kingdom, 2015

N. V. Gama, R. Santos, B. Godinho, C. S. R. Freire, R. Silva, A. Barros-Timmons, C. Pascoal Neto, A. Ferreira, "*Polyurethane foams from crude glycerol*", Poster communication, XI CICECO Meeting – Aveiro, Portugal, 2015

Patents

A. Ferreira, B. Godinho, R. Santos, **N. V. Gama,** R. Silva, A. Barros-Timmons, "Desalinization of crude glycerol", Patente Internacional - WO 2017/001892 A1

A. Ferreira, B. Godinho, R. Santos, **N. V. Gama,** R. Silva, A. Barros-Timmons, "Desalinization of crude glycerol", Patente Nacional - P302-5PP

A. Ferreira, **N. V. Gama,** B. Soares, C. S. R. Freire, A. Barros-Timmons, C. Pascoal Neto, R. Silva, I. Brandão, "Method for production of rigid polyurethane foams using unrefined crude glycerol", Patente Nacional - 107711 E, 2014/06/12

Contents

Objectives

Rigid PUFs are normally used as thermal insulation materials for construction but its sustainability, as well as the enhancement of their properties must be improved. In that sense, in this PhD project several goals are aimed to increase the acceptability of PUFs by the consumers, namely:

(i) The scientific community has been paid more attention in the use of CG in the production of PUFs, nevertheless the variability of its composition can be a drawback, so the primary goal of this project is to evaluate the influence of the CG composition on the properties of PUFs. This can be achieved by using different CG samples and evaluate its effect on the properties of PUFs.

(ii) Despite of their application, the optimization of the PUFs formulation, as well as, the establishment of the relationship of the PUFs formulation with the properties of the foams must be achieved. This can be achieve be using different PUFs formulations and statistically evaluate the effect of the reactant contents in the properties of the PUFs.

(iii) Compared with other thermal insulation materials, PUFs are already highly competitive, however if materials with the capability to absorb and release energy, the thermal efficiency of PUFs will be increased. And this can be achieved by the addiction of phase-change materials (PCMs). Moreover, due to the lower thermal conductivity of PUFs, to enhance the efficiency of the PCMs, the thermal conductivity of PUFs must be increased by the addition of a conductive agent, such as the expanded graphite (EG).

(iv) As well as almost organic materials, PUFs burns very easily and due to the greater attention paid to the fire safety of materials, the reaction to fire of the PUFs must be improved and this can be achieved by the addition of a flame retardant, such as EG.

(v) Normally, the better sound absorption properties are related with the open cells flexible PUFs. On solution to turn the rigid PUFs in a value-added materials, is to improve their sound absorption properties. This can be achieved by the partial substitution of CG by other eco-friendly polyol: polyol derived from the liquefaction of the coffee grounds.

(vi) The main disposal methods of PUFs wastes are land field and incineration. However, due to ecological reasons, these methods are no valid options. Despite of several chemical recycling methods are reported in literature, it is emerging a new method, the acidolysis, which convert the PUFs wastes into a reactant, which can be used in the production of new PUFs. In that sense, the successful recycling of PUFs by the acidolysis can improve the sustainability of the PUFs industry.

List of abbreviations

Symbol	Designation
A	Volume of NaOH solution required for titration of the polyol
Av	Acid value
ANOVA	Analysis of variance
B	Volume of NaOH solution required for titration of the blank
c	Specific heat capacity
C	Heat capacity
CG	Crude glycerol
d	Thickness
D	Thermal diffusivity
DMA	Dynamic mechanical analysis
DoE	Design of experiments
DSC	Differential scanning calorimetry
E	Integrity
EG	Expanded graphite
EHC	Effective heat of combustion
FTIR	Fourier transform infrared spectroscopy
h	Heat transfer coefficient
H	Enthalpy
HRR	Heat release ratio
I	Insulation
$k_{conduction}$	Thermal conductivity coefficient by conduction
$k_{convention}$	Thermal conductivity coefficient by convention
$k_{radiation}$	Thermal conductivity coefficient by radiation
m	Mass of reactant
M	Resistance to mechanical impact
MDI	Methylenediphenyl diisocyanate
MONG	Matter organic non-glycerol
$\overline{M}_n$	Number average molecular weight
N	Normality of the NaOH solution
OH_{number}	Hydroxyl number

O_v	Open cells content
PCM	Phase change material
php	Parts per hundred polyol
POL	coffee grounds derived polyol
PU	Polyurethane
PUF	Polyurethane foam
$\dot{Q}$	Heat flux
R	Load bearing capacity
RIM	Reaction injection molding
R_{iso}	Isocyanate monomer
R_{polyol}	Polyol monomer
R_s	Sound reflected
S	Tightness
SEA	Specific extinction area
SEM	Scanning electron microscopy
T	Temperature
TDI	Toluene diisocyanate
TGA	Thermogravimetric analysis
V_{spec}	Volume measured
V_{geoc}	Geometric volume
W_{abs}	Sound absorbed
W_{inc}	Sound incident
α	Absorption coefficient
λ or k	Thermal conductivity coefficient
ρ	Density

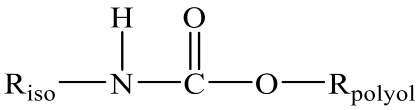
List of tables

List of figures

1. Introduction

Materials such plastic foams, foamed plastics, cellular plastics, or polymeric foams are materials that consists in a solid phase and a gas phase and one of the most important class of these materials are the polyurethane foams (PUFs).[1] Its durability and versatility properties lead to its use as domestic and industrial applications and even to space travel and medicine. For these reasons, the use of PUFs has grown impressively over the years.[1,2]

PUFs are polymers formed by the reaction between the OH groups of a polyol with the NCO groups of an isocyanate and its name is attributed to the repetition of the urethane linkage in its molecular backbone.[2–5] Where R_{iso} is derived from the isocyanate monomer, while R_{polyol} is derived from the polyol component.

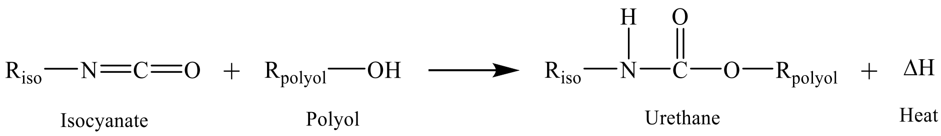


$$R_{iso}-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-R_{polyol}$$

Scheme 1 - Chemical structure of urethane [4]

The first urethane was synthesized in 1849 by Wurtz.[6] Afterwards, in 1937 Otto Bayer synthesized polyurethanes (PUs) from the reaction between a polyester diol and a diisocyanate.[2,5–7] Indeed this consisted in a major breakthrough at the time, as it consisted in a new class of polymerization reaction called polyaddition, also known as step polymerization.[5,6] Nevertheless, at first, this polymer was considered useless.[2]

The reaction between isocyanates and alcohols, is an exothermic reaction and leads to production of urethanes as described before and illustrated in Scheme 2.[3,6]



$$R_{iso}-N{=}C{=}O + R_{polyol}-OH \longrightarrow R_{iso}-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-R_{polyol} + \Delta H$$

Scheme 2 - Reaction scheme of urethane production [6]

Generally the polyol has several hydroxyl groups (between 2 and 3) in its backbone. Primary hydroxyl groups are more reactive than secondary hydroxyl groups and much more reactive than tertiary and phenolic as presented in Figure 1. 1:[6]

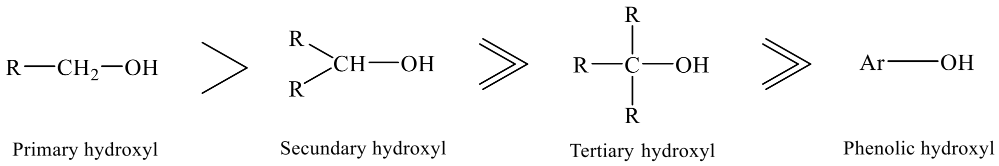
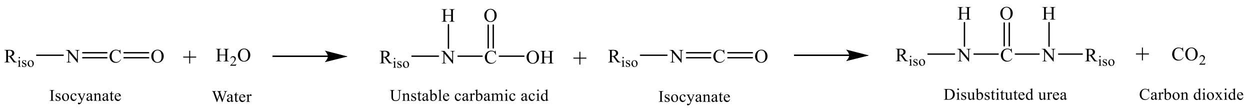


Figure 1. 1 - Reactivity of hydroxyl groups [6]

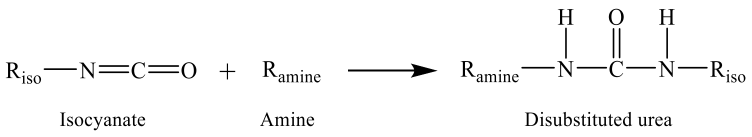
Along with this main reaction, others reactions may occur, such as: (*i*) the reaction of the isocyanate with water, which produce ureas and carbon dioxide (Scheme 3); (*ii*) the reaction of the isocyanate with amines, which produces urea (Scheme 4); (*iii*) the reaction of the isocyanate with urethane, which produces allophanate (Scheme 5); (*iv*) the reaction of the isocyanate with urea, which produces biuret (Scheme 6); and (*v*) the reaction of the isocyanate with carboxylic acid, which produces amide and carbon dioxide (Scheme 7).[3]

The reaction between isocyanates and water yields an urea group and carbon dioxide, which has a crucial role in the formation of the cellular structure of PUFs. This reaction is more exothermic than the reaction with polyols.[6]



Scheme 3 - Reaction scheme of the isocyanate with water [6]

The isocyanate reacts with water, which produces an unstable carbamic acid. Next, this molecule reacts with another isocyanate molecule generating a symmetrical disubstituted urea, meaning that one mole of water reacts with two NCO groups. This consideration must be in account to calculate the necessary amount of isocyanate. [6]



$$R_{iso}{-}N{=}C{=}O + R_{amine} \longrightarrow R_{amine}{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R_{iso}$$

Scheme 4 - Reaction scheme of the isocyanate with amine [6]

The amines are much more reactive than the hydroxyl compounds and depending on its substitution degree, have different reactivities. The reactive order is:[6]

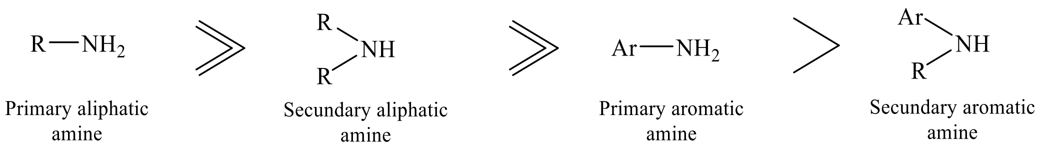
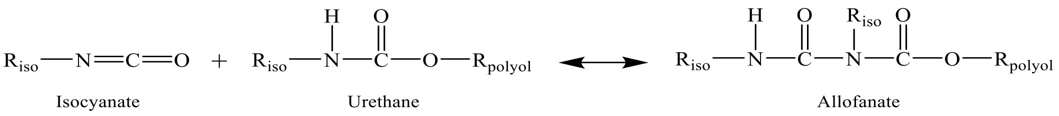


Figure 1. 2 - Reactivity of amines [6]

The urethane group is an hydrogen active compound (it has an hydrogen atom linked to the nitrogen atom), so it can react with another isocyanate group, forming an allophanate moiety.[6]

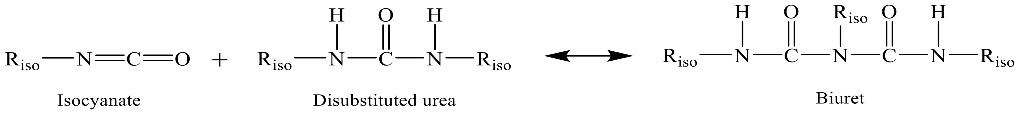


$$R_{iso}{-}N{=}C{=}O + R_{iso}{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R_{polyol} \longleftrightarrow R_{iso}{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{R_{iso}}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R_{polyol}$$

Scheme 5 - Reaction scheme of the isocyanate with urethane [6]

The carbonyl groups can withdraw electrons, turning the NH groups more reactive, allowing the formation of the allophanate.[6] Also, it is important to notice that the allophanate formation is an equilibrium reaction.

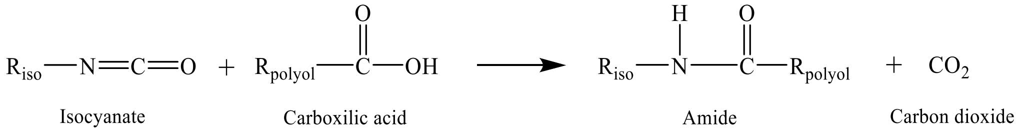
Similarly to the allophanate formation, the NH groups of urea react with isocyanates, to form a biuret.[6]



Scheme 6 - Reaction scheme of the isocyanate with urea [6]

As well as to the allophanate formation, the formation of biuret is an reversible reaction. The formation of allophanates and biurets, is a supplementary source of crosslinking.

The reactivity of isocyanates with carboxylic acids is lower than its reactivity with hydroxyls or amines and the final product is an amide group as well as carbon dioxide.[6]



Scheme 7 - Reaction scheme of the isocyanate with carboxylic acid [6]

As showed, the synthesis of PUFs is an intricate process because it involves several reactions. All of them compete with each other, however they have different reactivities. In Table 1. 1 are listed the relative reactivities of isocyanates with the different hydrogen active compounds.[6]

Table 1. 1 - Relative reactivities of isocyanates with different hydrogen active compounds[6]

Hydrogen active compound	Main hydrogen active product	Relative reaction rate (non-catalyzed, 25 ºC)
Primary aliphatic amine	Urea	2500
Secondary aliphatic amine	Urea	500-1250
Primary aromatic amine	Urea	5-7.5
Primary hydroxyl	Urethane	2.5
Water	Urea	2.5
Carboxylic acid	Amide	1
Secondary hydroxyl	Urethane	0.75
Urea	Biuret	0.375
Tertiary hydroxyl	Urethane	0.0125
Phenolic hydroxyl	Urethane	0.0025-0.0125
Urethane	Allophanate	0.0025

Nowadays PUs are used as every daily life products, being one of the most important class of polymers, changing the quality of the human life.[6] The wide range of its applications derived from the fact that their properties can be widely modified by selecting the raw materials, auxiliary reactants and their quantities.

The worldwide consumption of PU was estimated in USD 51 billion in 2015 and predict in over USD 77 billion by 2023 [8] and it represented in 2012, near 6% of the global consumption of plastics (Figure 1. 3).[9]

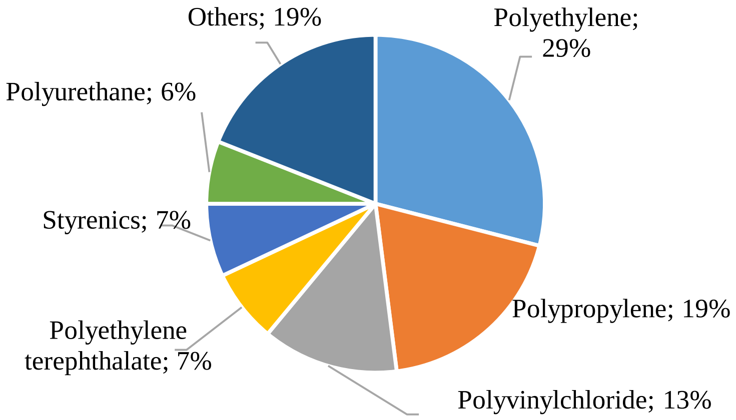


Figure 1. 3 - World consumption of plastics in 2012

The principal consumption of PUs is in the form of PUFs (Figure 1. 4).[9]

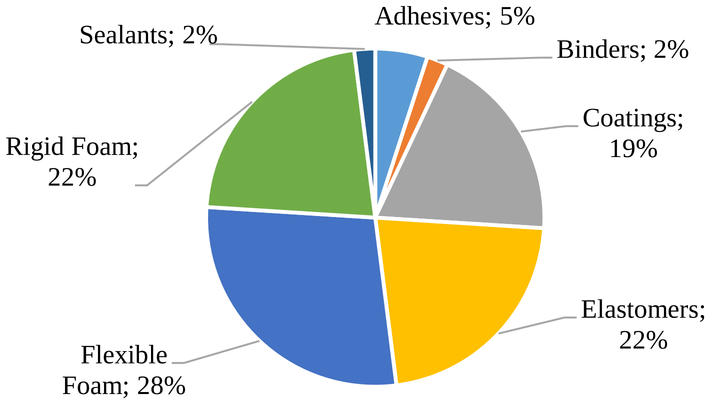


Figure 1. 4 - Global consumption of PU in 2012

Being a well-developed technology, the PUFs production represents over than half the of all polymeric foams production.[2] The main types of PUFs are the flexible foams and rigid foams, despite of other classifications can be attributed to PUFs, such as flexible PUs slab, flexible molded foams, reaction injection molding (RIM), carpet backing or two-component formulations, etc.[2,3] Despite that flexible foams and rigid foams derive from a similar chemistry, the differences of their properties are associated with the differences in their reactants characteristics, namely the polyols used. Normally, to produce flexible foams, is require polyols with a molecular weight of

2000-5000 g/mol and an OH number of ~50 mg_{KOH}/g, while to produce rigid foams, is require polyols with a molecular weight of 400-900 g/mol and an OH number of ~400 mg_{KOH}/g.

The PUFs are an expanded material and its expansion is a result from a combination of several processes. It stars from the mixing of the reactants, next a co-polymerization and an expansion occurs which involves at least the following steps:[1,10]

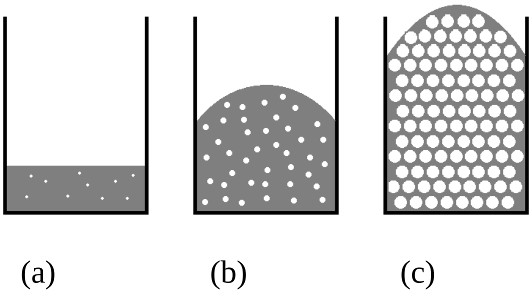


Figure 1. 5 - Representation of the stages of foam expansion: nucleation (a), cells growth (b) and stabilization (c)

- Nucleation - During the mixing air bubbles are introduced in the mixture. Theses bubbles are few and large and without the stabilizing effect of the surfactant, coalescence can occurs. The surface tension of the surfactant decreases the tendency of the gas to diffuse from the smaller to larger bubbles, which improves the homogeneity of the cellular structure. For this reason, this step has a paramount importance, since the cells of the final foam are derived from these air nuclei. Also, the number and size of these air nuclei are related with the mechanical energy provided in the mixing process.
- Cells growth - The cell growth can be derived from: (*i*) diffusion of blowing gas into existing bubbles. Notice that the mixture can be supersaturated with gas, which can leads to the dissolved gas begins come out of mixture. However, a reduced number of air bubbles lower the diffusion rate of the gas from the mixture to bubbles; (*ii*) expansion of the gas in the bubbles due to heat of reaction; (*iii*) diffusion of the gas from smaller bubbles to larger bubbles. The lower surface tension favors the reduction of the pressure difference between

bubbles of different size. This reduce the diffusion and promotes a smaller average cell size.

- Stabilization – the cell coalescence occurs when the liquid film separating two bubbles is ruptured. Once the cells are formed in the growing foam, they should be stabilized until the structures achieve sufficient strength through polymerization. However, several effect can rupture of the cell walls, such as temperature, drainage, and capillary action. This can be spread to other cells resulting in cracking, or total collapse of the foam. Once again, the surfactant has a paramount importance, because it stabilize and reduce surface tension gradients.

These steps have particular characteristics and can be monitored by:

- Cream time: which is the time when the volume starts to increase.
- Gel time: which is the time when the foam is dimensionally stable and has developed enough strength to resist finger impressions.
- Fiber time: is the time when the reaction mix transits from the liquid to the solid state which means that the reaction is about 50 % complete. The fiber time is measured by, for example, immersing and removing repeatedly a wooden rod from the expanding mixture, and it is determined when the rod draws fibers.
- Rise time: which is the time when stops the increase of the volume. In other words, is the time when the expansion process ends.
- Tack-free time: which is the time when the surface of the foam is no longer adhesive.
- Curing: which is the time when the material solidifies.

As mention PUFs are cellular structures, obtained by the expansion process during the PU polymerization reaction. The reactant that provides the gas is the blowing agent.[2] There are two main types of blowing agents: (*i*) physical blowing agent (such as solvents with low boiling point) which expands the polymer by vaporization; (*ii*) chemical blowing agents (such as water), which expands the polymer by the CO_2 produced.[11] Moreover, the cells can be derived from others sources: namely, dissolved gases in the reactants or gases released from thermally decomposable additives. Despite the source, the number and size of the cells are important because it affect all PUFs properties.[1]

The PUFs production is a complex process, which requires cautions to overcome possible defects on the final material which ultamitly can compromise its application. Some possible defects are:

- Loose Skin – when the adhesion between the skin of PUF and mold is greater than the cohesion of the skin to the foam body the PUFs. This problem be minimized by increasing the amine catalyst and/or increase the isocyanate concentration or eventually increase the mold temperature.[12]
- Foam Shrinkage - Foam shrinkage can be due to the polymerization being too fast compared to the expansion or due to an incorrect mixer speed (too fast or too slow). To overcome foam shrinkage the amount of tin catalyst can be reduced and/or the amount of amine increased, or adjusting mixer speed.[12]
- Foam Collapse – The partial or total foam collapse can be due to the foaming reaction being too fast. If the gas-generation rate is too fast the amount of amine catalyst needs to be reduced.[12]
- Scorching - Scorching is an undesirable discoloration phenomenon due to thermal degradation, causing the foams to assume a yellow to brown color. This discoloration is especially apparent in the center of the blocks where the internal temperatures remain high for a relatively long period of time. This effect can be reduced by adding to the mixture UV absorbers, antioxidants or optical brighteners.[13]
- Blow Holes - Blow holes can be due to the air trapped in the reaction mixture, as a result of the gel reaction being too fast or of the temperature of the blowing agent too high.

Reducing height between mixing head and mold can prevent air trapped in the mixture, reducing the concentration of tin catalyst can reduce the gel reaction time and reducing the blowing agent temperature prevents premature volatilization and reduction of vapor pressure.[12]

- Void Formation - To obtain a regular structure and to prevent void formation, the reactants must have the correct amount of suspended gas required to nucleate cells. Large closed cells are formed if too little nucleation occurs while smaller cells are formed if too much nucleation takes place.[12]

Depending on the formulation, a wide range of densities and mechanical properties can be obtained for PUFs. Also open cell foams, closed cell foams or both can be produced. Open cell foams have interconnected cells, which allow the passage of a gas from one cell to others. Closed celled foams do not have interconnected cell openings, so gas is trapped inside the cells. Examples of open and closed cell foams can be seen in Figure 1. 6. Foams can also have a combination of open and closed cells within the same sample.

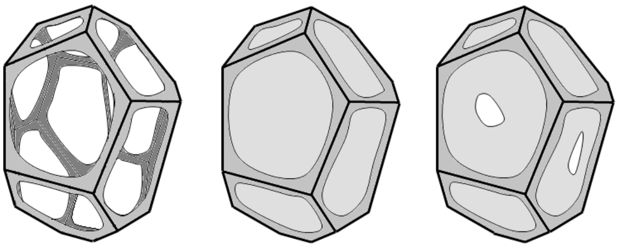

(a) (b) (c)

Figure 1. 6 - Porous structure of an open cells foam (a), of a closed cells foam (b) and open/closed cells foam (c) (adapted from [14])

Normally, open cells foams are appropriate for sound insulation applications, while closed cells foams are appropriate for thermal insulation applications. The thermal insulation is primarily due to a combination of cell size and cell morphology which trap the low thermal conductive gas inside. Within this spectrum, closed cell rigid foams are an important class of materials due to their outstanding thermal insulation properties. In addition, its high mechanical strength, their strong adhesive propensity, or their easy processing, makes rigid PUFs an attractive choice in various industrial applications, such as refrigerators and sandwich panels where rigid PUFs dominate the market.[1]

Despite of the excellent properties of the PUFs, it is common to prepare PUFs composites in order to improve their properties. Besides the thermal insulation, reaction to fire and sound absorption properties, which will be discussed below, other properties such cellular structure, mechanical resistance, the susceptibility to fungi in a wet environment, electrical conductivity, can be improved by the addiction of functional fillers. The use of these fillers increase the range of the applications of conventional PUFs, beyond construction and automotive industry to radar absorbing and EMI shielding, oil absorbents, sensors, fire proof, shape memory or biomedical materials.[15]

Different types of fillers, such as cellulose and lignocellulosic fibers,[16,17] glass wool, glass microspheres or glass fibers,[18–20] egg shell wastes,[21] date palm particles,[22] walnut and hazelnut shells,[23] esparto wool,[24] just to mention a few, can be used to improve the structural and mechanical properties of PUFs. Despite of having, as well a significant effect on the structural and mechanical properties, materials such as carbon nanotubes,[25–28] graphene,[29–32] or inorganic fillers, such as Fe_3O_4,[33] TiO_2,[34] iron oxide[35] are commonly used to increase both thermal and electrical conductivity of PUFs.

The addition of fillers in PU matrix may influence the processing parameters of the polymer, thereby affecting the formation of the foam. Nevertheless PUFs composites with enhanced properties can reduce the weight, energy, and cost of the material/application.

As mentioned, PUFs presents a wide range of applications which is derived from the fact that their properties can be widely modified. In that sense, its properties must be determined properly.

Scanning electron microscopy (SEM) analysis is an important and versatile tool to inspect the foam structure. SEM analyses is performed using a scanning electron microscope after vacuum-coating with gold to avoid electrostatic charging during examination and at accelerating voltage of (normally 15.0 kV). SEM images can also be used to determine the average cells size of the foams, by inspecting visually at least 15 porous cells on the surface of the each foam.

The porosity of the foams is also an important parameter because has significant effect in almost every property. Its determination is carried out using a gas pycnometer instrument by the nitrogen adsorption of samples (at 77 K). The samples must be outgassed overnight prior to adsorption measurements. The Brunauer-Emmett-Teller (BET) model is applied to fit the nitrogen adsorption isotherms and to calculate the specific surface area of the samples.[36] The pores volume and their diameters are calculated according to the model developed by Barret, Joyner e Halenda (BJH).[37]

The open cells content (O_v) is another important parameter (by definition, an open cell is a cell which is not totally enclosed by its walls and it is open to the surface either directly or by interconnecting with other cells [38]) and is determined in accordance with the ASTM D6226-05 standard [38] using a gas pycnometer instrument. This device uses a calibrated test chamber and known pressures and volumes of helium to calculate the permeable volume of the test specimen. By comparing the volume measured (V_{spec}) with the test instrument to the original geometric volume (V_{geo}), the open cells content can be determined using Eq. 1.

$$O_v = (V_{geo} - V_{spec})/V_{geo} \times 100 \qquad \text{(Eq. 1)}$$

Typically, rigid PUFs used as termal insulation materials present 93-97% of closed cells content.[39]

Density also affects the thermal and mechanical properties of PUFs, among others. For the density measurement, PUFs specimens with specific dimensions are weighed. The density of PUFs usually ranges from as low as 30 kg/m^3 to 100 kg/m^3.[40] Density is then obtained, dividing the weight of the specimens by the volume. To an accurate measurement of the density it is required to determine at least 10 specimens. Moreover, it can be necessary to determine the density of the button, middle and top of the foams.

The thermal conductivity (k) is a property of paramount importance which can determinate the application of PUFs. Typically rigid PUFs have a thermal conductivity of 0.016 – 0.023 W/m.k, but is very dependent of its density.[41] The determination of the thermal conductivity, can be carried out by introduced a thermal conductivity sensor inside the foams and the obtained value, is registered. Once again, it can be necessary to determine the thermal conductivity in various regions of the foams and the values obtained averaged.

Compressive tests are performed to study the mechanical properties of the PUFs. It is carried out according to the ASTM D 695 [42] using an universal mechanical test analyzer. Usually, before analysis, PUFs specimens are conditioned at 20 ºC and 41% relative humidity, in a chamber with humidity control, for 24 h. Samples are then placed between the two parallel plates and compressed at 10 mm/min (100%/min) up to 30% of compression. The Young modulus can be calculated by the slope of the tangent of the linear portion up to 5 % strain (where elastic deformation occurs) of the stress–strain curve. The compressive stress is the stress at which the plastic deformation begins to occur. Toughness was calculated by measuring the area underneath the stress-strain curve (up to 30% of strain). To an accurate measurement of the mechanical properties it must be required to determine at least 10 specimens of each foam and in different regions of the foams. Moreover, due to the anisotropy of the foams, the samples must be placed in the compressive plates in the expansion orientation.

Dynamic mechanical analysis (DMA) is carried out in order to obtain further information on the viscoelastic properties of PUFs. Samples with dimensions of 10 x 9 x 6 mm^3 are normally compressed from -55 ºC up to 150 ºC at a constant heating rate of 2 ºC/min and at a frequency of 1 Hz. Again, due to the anisotropy of the foams, the samples must be placed in the compressive plates in the expansion orientation.

Differential scanning calorimetric (DSC) analyses is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Before the analysis the sample must be ground to obtain a fine powder. Next, both the sample and reference are maintained at nearly the same temperature throughout the experiment is carried out within a specific temperature range and a heating rate of 5 ºC/min.

Another important issue of all materials, especially renewable materials, is their thermal stability, hence thermogravimetric analysis (TGA) analysis must be carried out using a thermogravimetric analyzer, from room temperature up to 800 ºC, at a heating rate of 10 ºC/min and under oxygen flux (200 mL/min).

1.1. Renewable polyols for the production of PUFs

As previously mentioned, the two main reactants involved in PUFs production are the polyol and the isocyanate. Polyols are liquid oligomers or polymers which have at least two hydroxyl groups (generally they present a functionality between 2 and 3), being the major types of polyols polyether or polyester polyols.[3,4,43] Figure 1. 7 illustrate the typically structure of polyether and polyester polyols.

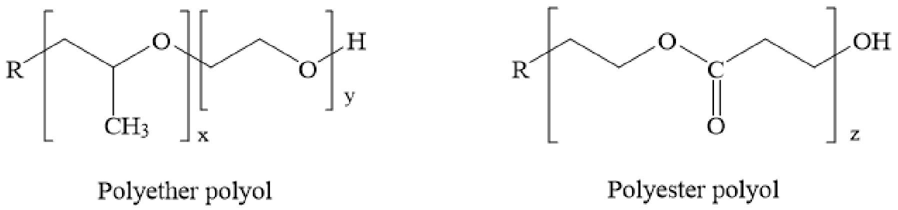


Figure 1. 7 - Typical structure of segments of polyether and polyester polyols

Several properties of foams can be controlled by varying the functionality of a polyol. For example, increasing the polyol functionality without changing the molecular weight produces a slight increase in foam hardness and a small reduction in tensile strength, tear strength and elongation. Also, the time at which the gel point occurs decreases. In turn, increasing the equivalent weight of the polyol (molecular weight divided by the functionality) while maintaining the functionality of a polyol, increase tensile strength and elongation.[43] In that sense, the characteristics of the polyols must be determined.

The acid value (AV) is determined in accordance with the ASTM D4662 standard.[44] Approximately 2 g of polyol is dispersed in 50 mL of ethanol in a 100 mL Erlenmeyer flask. Titrations is conducted using 0.1 N NaOH solution and the end point determined by a digital pH meter or using phenolphthalein as indicator. The number of milligrams of KOH required to neutralize the acid of one gram of the polyols is calculated using Eq. 2.

$$AV = (A - B) \times 56.1 \times N/m \qquad \text{(Eq. 2)}$$

where A is the volume of NaOH solution required for titration of the sample (cm^3); B is the volume of NaOH solution required for titration of the blank (cm^3); N is the normality of the NaOH solution; and m is the weight of the sample (g). The analyses were performed in triplicate and the results averaged.

The hydroxyl number (OH_{number}) is determined in accordance with the ASTM D4274 standard in which the esterification process is catalyzed by imidazole. Titrations are conducted using 0.5 N NaOH solution and the end point determined by a digital pH meter or using phenolphthalein as indicator. The OH_{number} is calculated according to Eq. 3.

$$OH_{number} = ((A - B) \times 56.1 \times N)/m + AV \qquad \text{(Eq. 3)}$$

where A is the volume of NaOH solution required for the titration of the sample (cm^3); B is the volume of NaOH solution required for the titration of the blank (cm^3); N is the normality of the NaOH solution; m is the weight of the sample (g); and AV is the acidity of the sample (mg$_{\text{KOH}}$/g). The analyses were performed in triplicate and the results averaged.

The number average molecular weight ($\bar{M}_n$) of polyols can be measured using Vapor Pressure Osmometer calibrated using four standard solutions of benzil in acetone, at 40 ºC, in the concentrations range of 4.5883 g/L up to 20.6790 g/L. The analyses are performed in triplicate and the results averaged. $\bar{M}_n$ can also be determined using Eq. 4:

$$\bar{M}_n = (f \times 56100)/(AV + OH_{number}) \qquad \text{(Eq. 4)}$$

Where f is the functionality of the polyol.

The determination of the water content is carried out using a Coulometer for Karl Fisher titration, according ASTM D6304.[45] The samples of polyols are analyzed using Hydranal (Hydranal Coulomat AG, Sigma) as reagent. The analyses are performed in triplicate and the results averaged.

Viscosity is normally measured using a rheometer, accordingly ASTM D4878.[46] Measurements are carried out using a coaxial cylinder and samples must be held isothermally at 25 °C throughout the measurements. The viscosity is determined at a constant shear rate and the measurements are carried out at least in duplicate.

So far, most of these polyols are derived from petroleum feedstocks but the increasing concern over environmental impact and scarcity of petroleum, has motivated the development of PUFs from bio and renewable raw materials.[47] The growing interest for the use of renewable materials has led to the increasing of the use of renewable and sustainable products, like green and bio polyols, for the production of PUFs. Green and bio polyols market is expected to worth USD 4.7 Billion by 2021, being the North American region, the largest market for green and bio polyols, in terms of both, value and volume.[48] This is due to the growing preference for the use of materials that have a lower carbon impact, that are recyclable or derived from non-polluting resources. Renewable polyols are thus an obvious alternatives for petroleum-based polyols. Companies such as Dow Chemical, Bayer Material Science, BASF SE or Shell Chemicals Ltd are already commercialize bio-based polyols.[49] Moreover, extensive research has been concentrating on developing bio-based polyols from renewable sources, such as biomass residues, vegetable oils or industrial by-products (Figure 1. 8). [50–54]

Figure 1. 8 - Renewable feedstocks for the production of PUFs

The increase of this research can be expressed by the percentage of publications related to the use of renewable feedstock for the production of PUFs in the last 20 years (Figure 1. 9).

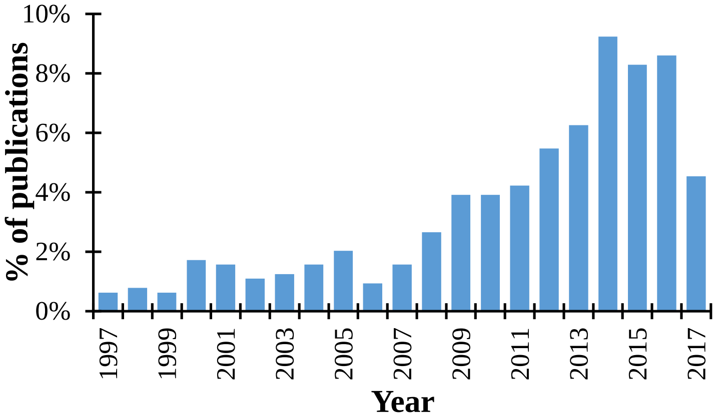


Figure 1. 9 - Percentage of publications related to the use of renewable feedstock for the production of PUFs

Processes such as oxypropylation [55] or acid liquefaction [56] of biomass feedstocks have been used to produce renewable polyols for the PUs industry. The results demonstrated that replacing, at least partially, the typical petroleum-based polyol with these types of materials, foams had comparable foaming kinetics, density, cellular morphology and thermal conductivity.

The oxypropylation of the biomass involves an initial degradation process which is followed by polymerization that forms grafts of poly(propylene oxide).[55] It consists in the ring-opening and anionic polymerization of oxiranes. In other words, it consists in grafting and chain-extension of macromolecular structures containing hydroxyl groups.[57] The oxypropylation does not increase the number of hydroxyl groups but increase the functionality of the final product.[57]

The oxypropylation can be carried out by a single step or by a two-step process. Both involves functionalization and oxypropylation of the biomass, which can be performed simultaneous or separately.[58] In the two-step process, first the biomass is impregnated with an alkaline solution (normally a strong Brønsted base – KOH in ethanol), under N_2 atmosphere and pressure. Its objective is to increase the reactivity of the hydroxyl groups present in the biomass.[57] In the second step, the propylene oxide is added to the functionalized biomass, occurring the formation of oxyanion groups at the end of the chains and subsequently polymerization.[59] When the propylene oxide is all consumed, the pressure decrease, meaning the end of reaction. In the single oxypropylation step, also occurs the homopolymerization of the propylene oxide, so in both cases the final product is a mixture of oxypropylated biomass, unreacted biomass and poly(propylene oxide). Their relative amounts in the final product are strongly related with the biomass granulometry, catalyst/biomass ratio, propylene oxide/biomass ratio, functionalization conditions, temperature, pressure and time.[60]

The oxypropylation of biomass or biomass derived compounds like sugar beet pulp,[61–63] cork,[64–69] chitosan,[70] corn starch,[71] data seeds,[72] rapeseed cake residue,[73] olive stone[74] and lignin,[75–78] among many others, were carried out successfully and used to produce PUFs.[55]

Ning Yan *et al.* [79] synthesized bio-polyols through the oxypropylation of bark. Afterwards, the ensuing polyol was used in the production of PUFs. A bark pretreatment was used, which consisted in activate the biomass with a solution of KOH in ethanol, during 1h at 100 ºC and 50 psi. After dried, the pretreated bark and propylene oxide were added to a reactor and the reaction was carried out during 2h at 180 ºC. The reaction presented an yield of 79% and the ensuing polyol an hydroxyl number of 444 mg_{KOH}/g. To demonstrate the potential of oxypropylated bark-based polyols in the production of rigid PUFs, the bark oxypropylated derived foam was compared with polypropylene glycol/glycerol derived foam and it was reported that the bark derived foam presented higher elastic modulus and compression strength.

Luc Avérous *et al.* [80] used gambier tannin-based polyols, obtained by oxypropylation process, in the production of PUFs. The tannin was pre-activated using a KOH solution and the oxypropylation temperature was 150 ºC and reaction was considered to be complete when the pressure returned to nearly zero. The oxypropylated tannin polyol presented an hydroxyl number of 256 mg_{KOH}/g and was used as replacement of commercial polyols. The resulting foams were extensively characterized and it was reported that besides of having similar kinetics, using higher contents of oxypropylated tannin polyol, the resulting foams presented higher closed cell content and compression strength at 10% deformation, as well as lower thermal conductivity. Also the flame resistance behavior was improved, with the addition of the oxypropylated tannin polyol.

Although oxypropylation is a suitable process to produce alternative polyols for the production of PUFs, as it requires propylene oxide, it is necessary homologated equipment capable of ensuring safety conditions against explosions provoked by sudden uncontrolled exothermic polymerizations.[57]

It is therefore much safer to use another process of converting biomass into polyols, such the acid liquefaction. The acid liquefaction technique is very attractive because do not require the use of high pressures or hazardous reactants such propylene oxide. The acid liquefaction of different kinds of biomass such as corn stalk,[81] lignin cellulosic compounds,[78,82–86] wheat straw,[87] cork,[88–90] corn,[81,91,92] bamboo,[93,94] data seeds,[72] eucalyptus and pine woods,[95] sugar-cane bagasse[96] or spent coffee grounds[97] among many others, has been successfully carried out as well.

The acid liquefaction operates under moderate temperatures (~160ºC) and at low or even under atmospheric pressure.[98] The acid liquefaction of lignocellulose materials uses liquefying solvents such as phenols or polyhydric alcohols and catalysts such as organic or inorganic acids.[56] In contrast to the oxypropylation, the liquefied product has higher OH number.[98] However, the process of biomass acid liquefaction can be very complex, because smaller compounds are produced by hydrolysis, dehydration, dehydrogenation, deoxygenation and decarboxylation, rearrangements through condensation, cyclization or polymerization, leading to new compounds.[98] Nevertheless, the degradation and repolymerization are the principal reactions that occur in the acid liquefaction. Despite the complexity of the reaction mechanism, the acid liquefaction is an effective method to convert biomass into polyols.

The residue content of the final product is one important issue for the acceptability of the biomass acid liquefaction and is highly correlated with the reaction conditions such as biomass/solvents ratio, biomass/catalyst ratio, reaction time and temperature.[56] Degradation makes the biomass to decompose and reduces the residue percentage, whereas repolymerization of the degraded products results in an insoluble materials which increases the residue content. At the beginning of reaction the degradation plays a more important role, resulting in the decrease of the residue content. In turn, at the following stage, the repolymerization has higher influence, because it is enhanced by the increase of small molecules derived from the degradation stage, which repolymerized into the insoluble polymer. So, the residue content drops at an initial stage and can increases after that. Therefore the acid liquefaction time is one of the most important factors affecting the residue content.

Mona Nasar *et al.* [96,99] optimized the sugar-cane bagasse liquefaction process and subsequently used this biomass derived polyol in the production of PUFs. Mixtures of ethylene glycol and phthalic anhydride were used as solvent and the optimal conditions for the liquefaction were 160°C during 180 minutes. The effect of partial replacement of polyethylene glycol by the sugar-cane bagasse derived polyol in the properties of PUFs were addressed and was reported that the foam density and compressive strength were improved with increasing of biomass-based polyol content. Also the presence of the sugar-cane bagasse derived polyol decreased the thermal conductivity of the foams.

Hong-Zhang Chen *et al.* [87] liquefied wheat straw for the preparation of biodegradable PUFs. It was used glycerol as solvent and the effect of the liquefaction reaction conditions were evaluated (influence of temperature, solvent/wheat straw ratio, catalyst content and water content of wheat straw). The optimal conditions were achieved using a solvent/wheat straw ratio of 6:1 and sulfuric acid of 5%, at 140 ºC during 2h and the ensuing polyol presented an hydroxyl value of 46 mg_{KOH}/g. The foam prepared using the liquefied wheat straw polyol was compared with a glycol based foam and it was reported that the apparent density, resilience rate, elongation and the tensile strength were similar. Additionally, the water absorption of wheat straw derived PUF was much higher and presented a good biodegradability. The degradation velocity essays shown that the wheat straw based foam presented a mass loss of PUF was 16%, while the glycol derived foam had a very little mass loss at the same conditions.

Others eco-friendly raw-materials can be used as polyols in the production of PUFs. Vegetable oils are abundant and a very important resources for polyols. They have carboxyls, esters, double bonds, active methylenes, hydroxyls, oxirane rings and others, which are suitable for the production of polyesters, alkyds, epoxies, polyethers, polyesteramides or PUs.[100]

Different kinds of vegetable oils have been used in the production of PUFs such as castor oil,[101–112] palm oil,[113–116] soybean oil,[47,117–127] rapeseed oil,[128,129] canola oil,[130] tung oil,[131] among others. They have versatile composition and structure, are biodegradable and environmentally friendly, are soluble in most of the industrial solvents allowing blending with conventional petrochemical-based polyols and the resulting foams exhibit good properties such as flexibility, mechanical strength, abrasion resistance, toughness, adhesion, chemical and corrosion resistance.[132]

An important class of vegetable oils for the production of PUFs are those unsaturated, such as soybean oil, sunflower oil, safflower oil, corn oil, linseed oil, olive oil, tung oil, castor oil and others, because the double bonds can be converted into hydroxyl groups.[6]

A unique vegetable oil is castor oil, which is the triglyceride of ricinoleic acid and had a paramount important at earlier stages of the PU industry, even before petroleum derived polyols were used. It is extracted from the seeds of the plant *Ricinus communis*, has 18 carbon atoms, a secondary hydroxyl group (C_{12}) and a double bond (C_9-C_{10}). It has a functionality of around 2.7 OH groups/mol and an hydroxyl number of around 160 mg $_{KOH}$/g. It can be used in almost every PU applications such as: coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants, adhesives, flexible foams and so on.

Yonghong Zhou *et al.* [133] synthesized castor oil-based flame retardant polyols. The castor oil was alcoholyzed with glycerol and the epoxidation of castor oil was carried out by formic acid and hydrogen peroxide. Afterwards a ring-opening reaction with diethyl phosphate and the modified castor oil was used in the production of PUFs. The thermal degradation and fire behaviour of PUFs were investigated by limiting oxygen index, cone calorimetry test and thermogravimetry analysis. It was reported that the foams presented regular cells size and the compression strength of PUFs was improved with the increase of flame-retardant polyols. Moreover the PUFs prepared from castor oil-based flame retardant polyol had excellent fire resistance.

Maria Kurańska *et al.* [134] studied the influence of rapeseed oil-based polyols on the foaming process of rigid PUFs and it was reported that the replacement of a petrochemical polyol by a rapeseed oil-based polyol affects the foaming process of PUFs by reducing the reactivity of the system. Moreover the increasing the content of rapeseed oil-based polyol resulted in a smaller decrease in the dielectric polarization which affects the gelling and foaming reactions.

Besides the use of bio-polyols, the use of industrial by-products, namely crude glycerol (CG) has been explored as polyol to produce rigid PUFs. Glycerol can be obtained as sub product of many reactions, such the saponification or the hydrolysis of triglycerides.[135]

Considerable studies have been conducted to develop both chemical and biological processes to convert CG to value-added products, such as into hydrogen, dimethyl ether, ethanol, microbial oil, polymers and biopolymers, or used in ruminant diet, among many others.[136–147] Also, it can be used as a fuel or feedstock for chemicals, but it required several purification process, such as saponification, acidification, neutralization, membrane filtration, solvent extraction or activated charcoal adsorption.[148,149] Moreover, the feasibility of the conversion of CG to value-added derivatives, rely on several factors, such as production cost, process technology, suitable separation and purification, suitable CG feedstock quality or minimum catalyst deactivation problem.[150]

In addition, the successful replacement of petrochemicals by CG in the PUFs production has the potential to reduce their cost and environmental impact. The production of PUFs from CG might also contribute to alleviating the current CG glut and to improve the sustainability of the PUFs industry.

First, CG was used as replacement of the traditional polyhydric alcohols, in the acid liquefaction of biomass.[84,127,151–154] It was tested successfully as solvent in the acid liquefaction process,[155] as well as in combination with petroleum based polyols.[156] The characteristics of the obtained polyols, proved to be suitable for the application of PUFs.

Being a polyol itself, CG represents a potential raw material for the production of rigid PUFs [155] and a couple of processes regarding the treatment of CG and subsequent use in the production of PUFs have been patented.[152,154] As an alternative, CG has been used directly without any pre-treatment or purification step, in the production of PUFs (Figure 1. 10).[52]

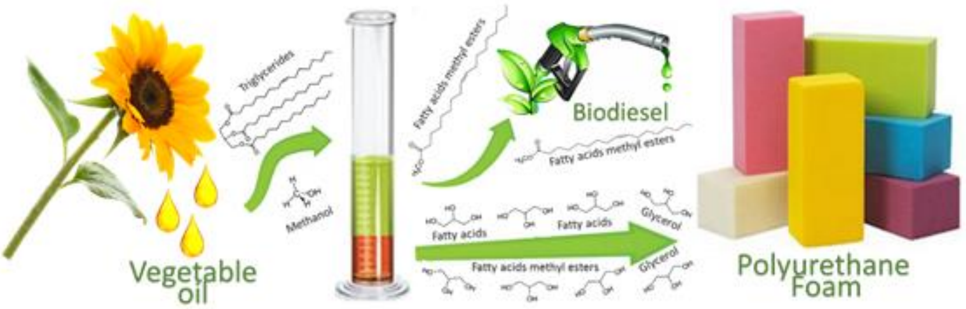


Figure 1. 10 - Process of the use of CG without any pre-treatment or purification step in the production of PUFs

As mentioned, typically the CG contains various impurities, including fatty acids, alkoxide salts, inorganic salts, "matter organic, non-glycerol" (MONG), water or unreacted methanol being its composition dependent of the feedstock used. Thus the variable composition of CG, can affect the properties of the ensuing PUFs.[157] For example, the presence of branched fatty acid and ester chains may help to reduce the degree of microphase separation and stabilize the bubbles during the foaming process.[157] This can result in a more homogeneous cellular structure, which can improve all physical properties. Also, the presence of methanol is particullary important because it can react with the isocyanate groups affecting the $R_{NCO/OH}$ and thus the crosslinking density, can be volatilized in toxic gases and may also lead to the hydrolyses of alkyl esters.

Due to the low average molecular weigth of CG, the polymer formed by the reaction of CG with aromatic isocyanate have high concentration of hard segments, which can increase the friability of the material as well as being associated with a high concentration of allophanates whci compromise the formation of quasi-polymers. Therefore, formulations need to be finelly tuned in order to produce PUFs.

To take the full advantage of the use of the CG without any purification step, the influence of CG composition on the PUFs properties must be determined. This can be assessed using CG samples with different composition and extensive characterization of the resulting PUFs in order to stablish a relation between the CG composition with PUFs properties, as will be discussed in Chapter 2.

1.2. Effect of the formulation on the properties of PUFs

The versatility of PUFs application arises from the fact that a wide range of properties can be achieved by small modifications on the formulation used. In that sense, it is common to adjust the type and content of the polyol, isocyanate, catalyst, surfactant, blowing agent and additives in order to control the properties of the ensuing foams.

Besides the effect of the type of polyol used, the nature of the isocyanate is equally important. The most commonly isocyanates used are the methylenediphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) and they have two or more isocyanate groups per molecule. They represent about 90% of the total diisocyanate consumption and are used to produce a wide range of PUFs products.[158]

Polymeric MDI (PMDI) is a mixture of MDI which contains 30 to 80 % (wt/wt) 4,4'-methylene diphenyl isocyanate and larger molecular weight oligomers of MDI. The term Polymeric MDI actually is not a polymer. It consists in a brownish liquid at room temperature, of molecular formula of $C_{15}H_{10}N_2O_2$ to $C_{47}H_{30}N_60_6$, molecular weight of 250.3-778 g/mol and is commonly used in the production of rigid PUFs.[158]

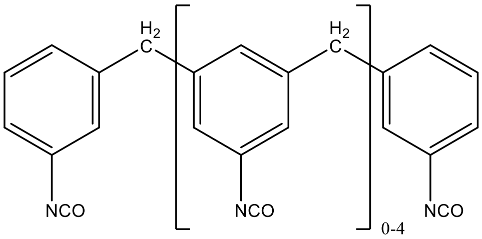


Figure 1. 11 - Typical structure of MDI

As mentioned before, the isocyanate reacts with the polyol producing urethane groups, and with water, producing urea groups and CO_2. Whilst the urethane and urea moieties are associated with the hard segments of PUFs, the polyol form the soft segments as illustrated in Figure 1. 12.[159] Therefore, higher isocyanate amounts yield more hard segments, making the PUFs more rigid. On the other hand, the use of higher isocyanate amounts also affects the foaming process associated with the release of CO_2.[11]

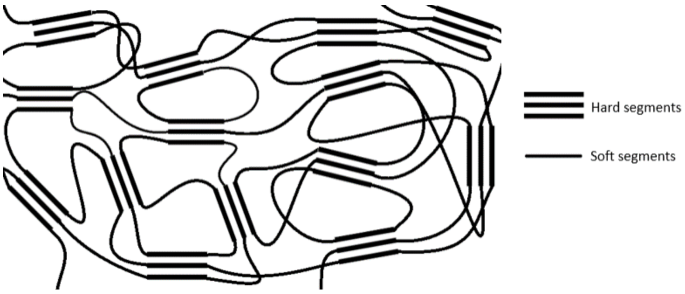


Figure 1. 12 - Representation of the structure of polyurethane (adapted from [6])

Though used in small proportion when compared to the polyols and isocyanate, another important reactant used in the production of PUFs is the surfactant. Silicone surfactants can lower surface tension, emulsify incompatible formulation ingredients, promote nucleation of bubbles, stabilize the cells and have significant effects on the cell size and foam air permeability.[1] They must also control the open cell content, preventing its rupture.

Finally, catalysts are used to promote the reaction between isocyanates/polyols and isocyanates/blowing agents. The most common catalysts are the amines or tin catalysts [4] and a proper expansion is obtained through a balance between polymerization (gelling) and gas generation (blowing). In that sense, the adjustment of catalyst type and quantity influence dramatically the expansion.

In order to study the influence of the PUFs formulation in the properties of the resulting foams, different amount of each reactant must be used and the resulting PUFs characterized. For this purpose, tools such as the design of experiments (DoE) should be used in formulation optimizations. This has actually been the case in the preparation of PUFs derived from coffee grounds polyol where the influence of the reactants quantities on the properties of the ensuing foams was reported.[51] Nonetheless, these influences must have statistical significance and analysis of variance (ANOVA) is a statistical tool that is commonly used to analyze the differences among and between groups (variables).[160] This tool has been applied for the evaluation and optimization of variables in different areas such: material science,[161] process parameters,[162] social behaviour,[163] meteorology,[164] among many other, and in the present project its use will be discussed in Chapter 3 in connection with the optimization of PUFs production derived from CG.

1.3. PUFs with enhanced thermal energy efficiency

As mentioned before, the main application of rigid PUFs is in the field of thermal insulation materials. Since PUFs are composed by a small portion of polymer whose thermal conductivity coefficient (λ *or* k) is in the range of 0.1-0.3 W/m.K [165] and a high portion of gas, which has lower thermal conductivity (λ ~ 0.0146 W/m.K [166]), the thermal conductivity of PUFs is much lower than that of the solid made of the same material.

Thermal insulation is associated with the reduction of the heat flux. In turn, the heat flux that passes throw the material can be defined as:

$$Q^{\cdot} = k/d\ (T_1 - T_2) \qquad \text{(Eq. 5)}$$

where $\dot{Q}$ is the heat flux in W/m^2 that passes from one face of the material to the other per m^2 area, k is the thermal conductivity coefficient of the material in W/mK, d is the thickness of the insulation material in meters, and T_1 and T_2 are the surface temperatures on the insulation material. k/d is also called the heat transfer coefficient for the insulation layer, or h, and is expressed in W/m^{2}K.[167]

The thermal insulation performance of a typical closed cells PUF filled with low thermal conductive gas, derives from three heat transfer phenomena: conduction, convection and radiation. In PUFs having an average cell size of no more than 0.5 mm, convection can be negligible.[168] However, to the diffusion of gases whith different densities out and/or into the foams, the heat transfer by convection may not be negligible. Yet, the heat transfer by conduction occurs trough the polymer (cell walls and struts (intersection of three cells)), and through the gas (which fills the interior of the cells). The heat transfer by radiation propagates practically only through the struts, since they are opaque, in contrast with the cells walls and the gas which fills the cells, since they can be considered transparent. In this kind of PUF, the heat transfer through the gas by conduction comprises 40% to 50% of the total heat transfer, whilst the heat transfer through the polymer by conduction and radiation comprises about 25% to 30% each one.[169] So the overall thermal conductivity coefficient, results from the sum of these contributions as expressed by Eq. 6.[1]

$$k = k_{conduction} + k_{convection} + k_{radiation} \qquad \text{(Eq. 6)}$$

where $k_{conduction}$ is the thermal conductivity by conduction, $k_{convention}$ is the thermal conductivity by convection and $k_{radiation}$ is the thermal conductivity by radiation (see Figure 1. 13). The coefficient of thermal conductivity is defined as the heat flow which takes place across a cube with 1 meter in cross-section and 1 meter in thickness, if the difference in temperature between the two faces is 1°C (W/mK).

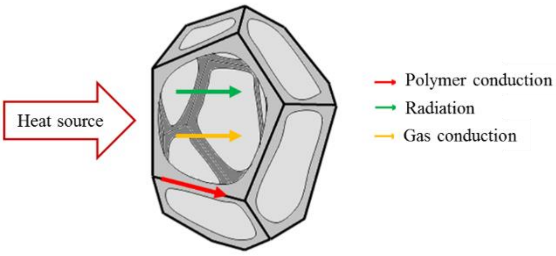


Figure 1. 13 - Representation of heat transfer in PUFs (adapted from [14])

In turn, the thermal diffusivity D (m^2/s) characterizes the heat conduction of a material, i.e. it describes how quickly a material reacts to a change in temperature and is related to thermal conductivity according to Eq. 7:

$$k = D\rho c \tag{Eq. 7}$$

where ρ is the density (kg/m^3) and c is the specific heat capacity (J/kg.K) of the material.

The foam cellular structure, i.e. density, the ratio of open/closed cells and the thermal conductivity of the gas used as blowing agent has paramount importance in the heat transfer phenomena. The lowest thermal conductivity of PUFs is obtained when there is a higher number of small closed cells ('voids'), because they trap the lower thermal conductive gas inside of the cells, reducing that way the heat transfer by convection.[167] Moreover, approximately 80% of polymer is in the struts (intersection of three cells), while the other 20% are present in the cells wall, so the heat transfer through conduction in the struts has great influence in the thermal conductivity by conduction of the material.[169] In a similar way, the thermal conductivity of the foams is related with its porosity. Since the porosity is the fraction of the total volume which is occupied by gas, as the porosity decreases, the thermal conductivity of the foams increases. The same applies to the cells size, as the cells size decreases, the conductivity of the foams approaches the thermal conductivity of the polymer.[169]

Besides conduction through the polymer, the heat is transferred by conduction through the gas.[169] The conduction by the gas is also dependent from the morphology of the foams. As the density increases or the cells size decreases, the gas conduction decreases slightly, but the overall thermal conductivity of the foam increases.

Finally, the heat transfer by radiation is the most difficult mechanism to understand properly. Like the previous mechanisms, the radiation is dependent from the foam structure. It consists of electromagnetic waves, which propagate through gases, liquids or solids.[168] The struts are opaque, which leads to high radiative heat transfer.[169] In contrast, the gas which fills the cells can be consider transparent, so the radiation occurs mainly due to the polymer. Since the heat transfer by radiation occurs through the polymer, the radiation can be decreased by increasing the extinction coefficient (the mean distance that a photon travels before it is absorbed or scattered) of the polymer. In that sense, changes in the polymer chemistry could be used, however PUFs produced from different reactants and formulations, present very similar extinction coefficients.

In brief, the overall thermal insulation of foams can be improved by a better control of the foaming process. Beyond that, if heat storage materials are incorporated into PUFs, the heat gain/loss, from/to the surroundings will be reduced and the energy saving will be much more efficient.[170–176] In the last years, this concept has found growing interest as a result of the rise of a new class of materials: the phase change materials (PCMs). PCMs, which are also called latent heat-storage materials, have high capability to store and release large amounts of heat energy within a slight or no temperature changes. In that sense, PCMs are often used as thermal regulation fillers.[177]

The sensible heat storage is the most common method for heat storage (ΔQ – W/m^2) [177] and can be determined by Eq. 8:

$$\Delta Q = C.\, \Delta T = m.\, c.\, \Delta T \qquad \text{(Eq. 8)}$$

Where, C (W/m^2.K) is the heat capacity of the material, m (kg) is the mass of the material and c (W/m^2.K.kg) is the specific heat of the material and ΔT (K) is the thermal amplitude.[177]

Additionally, energy storage can be obtained by the latent heat physical process, which is derived by the phase change process of the material. As Figure 1. 14 shows, for a solid-liquid phase change, when the melting temperature of the phase change is reached, the temperature of the PCM is constant and the stored heat increases.[177]

In the solid-liquid case, below and above the phase change temperature range, heat is stored as sensible heat and the temperature of the material increases. In turn, in the phase transition temperature, heat is stored as latent heat and the temperature is maintained constant. In other words, in the heating process, the solid-liquid PCMs change from solid to liquid, absorbing energy (endothermic process).[177] When the material cools down, the PCMs returns to its solid state, releasing the previously heat absorbed (exothermic process).[177]

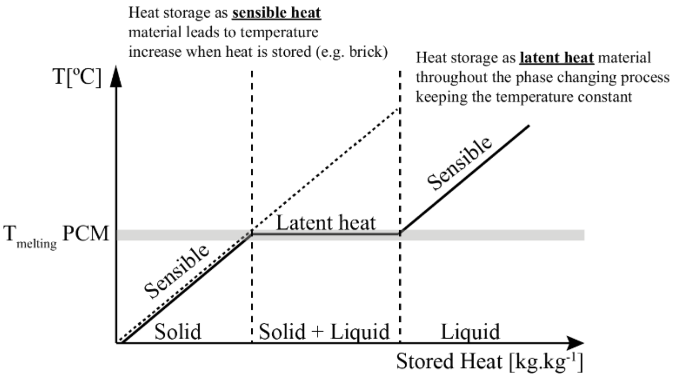


Figure 1. 14 - Latent heat storage for the case solid-liquid [177]

The latent heat storage at constant pressure can be determined from the enthalpy variation, ΔH (W/m^2) (Eq. 9):

$$\Delta Q = \Delta H \qquad \text{(Eq. 9)}$$

According to their phase change states, PCMs can be classified as: liquid–gas, solid–solid and solid–liquid PCMs. Liquid-gas transformation has the highest energy density, but the high volume variation, which makes difficult to store the gas phase, is a major drawback. [178,179] For that reason, materials used for thermal-energy storage are, typically, salt hydrates or paraffins. The advantages of solid-solid PCMs, such as molecular crystals, are that a liquid phase does not need be contained, so segregation of components does not occur.[180]

The most commonly used PCMs, are the solid–liquid phase transition, such as paraffin waxes, poly(ethylene glycol)s or fatty acids and their derivatives. In the heating process in solid–liquid PCMs, the energy is absorbed by the breakdown of the bonding responsible for the solid structure. A large amount of heat is absorbed during the phase change with no increase in temperature. In turn, when the materials cool down, the heat will be released to the surroundings as described in Figure 1. 15.[171,179,181–183] Outside the temperature range of the phase change process, the PCM behaves as a common material, storing sensible heat. [23]

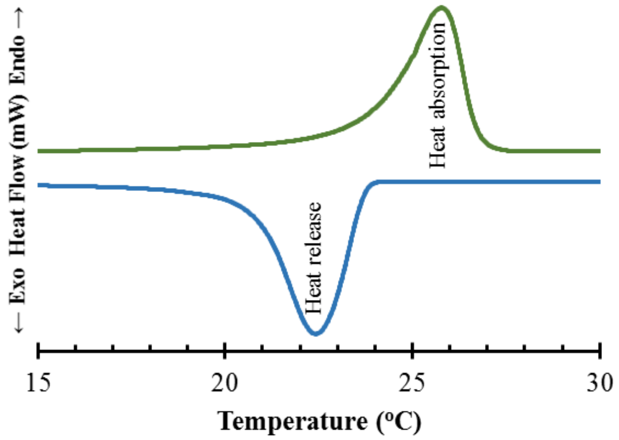


Figure 1. 15 - Action of PCMs

Numerous research groups have widely studied the thermal properties of paraffin waxes for the development of diverse heat storage materials. All these studies have shown that paraffin waxes absorb, store and release a great amount of heat and presents high latent heat storage capacities. They are chemically inert, noncorrosive, odorless, long lasting, inexpensive, easily available, ecologically harmless and nontoxic. Thanks to these outstanding characteristics, paraffin waxes have been extensively preferred for many commercial thermal storage applications.[184–187]

Even though the addition of PCMs is a strategy to enhance the thermal performance of PUFs, the low thermal conductivity of rigid PUFs requires the use of large and expensive heat transfer surfaces, which is considered as the major drawback in applying the PCMs in PUFs applications.[188] Hence, in order to improve the action of PCMs, the thermal conductivity of PUFs must be increased. One solution to overcome this problem is filling the polymer with conductive agents such electron-conductive fillers to form a network on the matrix of the polymer. Carbon based materials such as expanded graphite (EG) present several advantages over usual metal fillers due to lower costs, corrosion resistance, and ease of processing.[189] In that sense, the addition of EG allows to increase thermal conductivity and subsequently enhances the action of PCMs. Nonetheless, the lack of compatibility of EG and PCMs with the foams can disrupt the cellular structure, affecting all the properties of the foams and ultimately compromise its applications, so detailed studies must be conducted. Also, the use of PCMs has been widely studied, but still face a cost issue, constraining their use in large scale applications. Therefore, numerical simulation is essential in the framework for optimizing the composites formulations and thickness of the active layer containing PCM. These issues will be discussed in Chapter 4.

1.4. Reaction to fire of PUFs

Rigid PUFs as well as most organic materials burn very easily. Despite of that, for many years the fire performances of PUFs were suitable, but nowadays, the fire performances should be improved due to the greater attention paid to fire safety.

During combustion, PUFs generate highly toxic smoke, especially CO and hydrogen cyanide. The inhalation of these gases causes severe health problems or even death. Also, during a fire, there is a dramatic increase of temperature which leads to the decomposition of PUFs affording small molecules in the gaseous phase. The mixture of these small molecules with air forms a flammable mixture. In other words, when the concentration of this mixture and temperature cross the flammability limit, the material starts to burn.[190]

The behavior of a material with fire, can be classified by: (*i*) resistance to fire and (*ii*) reaction to fire. The fire resistance provides information about how well a building element, such as a wall, floor, door, etc, can maintain its properties when exposed to a fire. In order to be able to evaluate the behavior of different constructions and to compare the fire resistance of similar constructions, different time/temperature curves can be determined, the most common of which is the time-temperature curve defined in ISO 834-11:2014 adopted in most standards relating to resistance to fire.[191]

The resistance to fire of material is determined as the time to failure of one or more criteria, and can be classified as:

- Load bearing capacity R — the ability of a construction element to withstand fire exposure under specified mechanical actions, on one or more faces, for a period of time, without any loss of structural stability;
- Integrity E — the ability of an element of construction that has a separating function to withstand fire exposure on one side only, without the transmission of fire to the unexposed side as a result of the passage of flames or hot gases;
- Insulation I — the ability of an element of construction to withstand fire exposure on one side only, without the transmission of fire as a result of significant transfer of heat from the exposed side to the unexposed side.

Other criteria which are not linked directly to the use of insulation materials are: radiation W, smoke tightness S, and resistance to mechanical impact M, which provides the classification criteria for fire resistance tests in Europe.[192] Generation of smoke from building elements is not part of fire resistance criteria.

The reaction to fire is related with the instant after the beginning of a fire, its propensity to ignite or feed a fire. This behavior is assessed on the basis of standardized tests and described in a Euroclass classification.

In view of the increasing awareness of public opinion, the reaction to fire of PUFs needs be improved and this can be achieved by the incorporation of flame retardants. [190]

The flame retardance mechanisms physical and/or chemical thus, the use of different types of flame retardant can significantly change the flame retardance mechanisms.

Flame retardants can be used as additives or as reactive in order to interfere with combustion during different stages such as heating, decomposition, ignition, or flame spread. Halogenated paraffins and phosphorus containing compounds are a type common flame retardants.

The paraffinic compounds may not be very compatible with the PUFs and for that reason may jeopardize the mechanical properties of the materials besides releasing irritant acids. The phosphorus compounds, being a reactive type flame retardant can react with functional groups of PUFs. They act as char-forming agents, reducing the generation of flammable gases.[190] Reactive type flame retardants have the advantages of (*i*) increasing compatibility between polymer, (*ii*) not degrading the mechanical properties of the PU, (*iii*) possessing better compatibility as the flame retardant group is a part of the binder and (*iv*) using small amount or low concentration for the enhancement of fire-retardancy.[190]

A very distinct type of flame retardants are inorganic fillers. These materials produce a stable organic–inorganic interface, which reduces the concentration of decomposition gases and increases the diffusion path barrier of the volatiles produced during the degradation process.[190] Nowadays expandable graphite (EG) is widely used as flame retardant in PUFs. The role of EG as flame retardant is illustrated in Figure 1. 16.

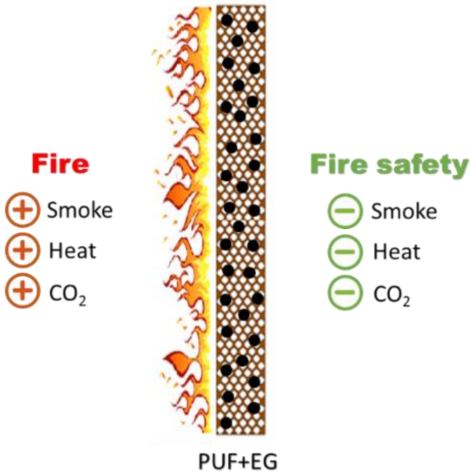


Figure 1. 16 - Effect of EG as flame retardant

Indeed, EG can effectively improve the flame retardancy properties of PUFs. Once exposed to heat, it forms a low density "worm" like structure on the surface of the PUFs that prevents heat and oxygen transfer, providing a good fire retardant performance.[190,193–195] The char layer, being a thermal barrier and thwarting oxygen diffusion, prevents further decomposition of the materials. Therefore, due to this protection effect, the presence EG can also decrease the mass loss rate and subsequently increase the residual mass of the PUFs after burned.

There are many others parameters that can be used to evaluate the reaction to fire of the materials. One of the most important is the heat release ratio (HRR). It represents a quantity of heat generated per unit area and time.[196] When a sample is ignited, heat is generated so the HRR is index to the extent of fire.[197] The effective heat of combustion (EHC), which is the ratio of the heat released to mass loss rate measured at a certain point, is related with the volatile gases formed during combustion.[198] The presence of EG can decrease the EHC value, meaning that the existence of EG prevents the combustion and release of heat, when the matrix is decomposed into the gas products.

As it is well known, compounds resulting from incomplete combustion are more toxic than those resulting from a complete one, therefore the CO/CO_2 weight ratio is an index of smoke toxicity. The physical barrier effect formed by EG, thwarts the oxygen diffusion favoring the development of products of incomplete combustion, like CO.[199] Consequently, the higher this ratio is, the higher the dangerousness of the material is when burned.

Another parameter of great importance that needs to be considered is the specific extinction area (SEA). It is related with the smoke density and as the lower the smoke density is, more easier it would be for people to escape from a fire.[196] Once again the presence of EG, can contribute to the decrease of the values of this parameter, meaning that it has an important role in the condensed phase.

Despite of all the advantages of EG, its use can compromise the cellular structure of the PUFs and therefore their mechanical properties, namely in the case of rigid PUFs such as those derived from renewable materials. This issue will be addressed in Chapter 5.

1.5. Sound absorption properties of PUFs

The extensive use of PUFs as construction materials is not just associated with their thermal insulation properties, but also with their sound absorber properties, especially for industrial applications, theatres, offices, sound studios and many other applications.[167]

The absorption coefficient (α) define the energy that is absorbed when a sound wave hits a material and is determined by the ratio of the sound absorbed (W_{abs}) to the sound incident (W_{inc}) (Eq. 10):[200,201]

$$\alpha = W_{abs}/W_{abs} \qquad \text{(Eq. 10)}$$

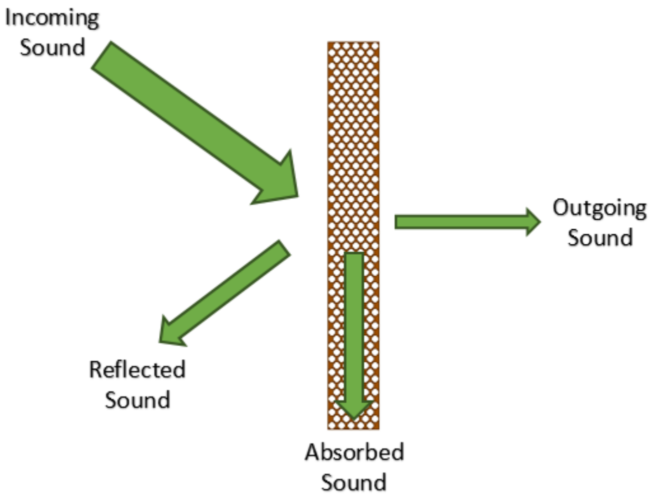


Figure 1. 17 - Schematic illustration of sound waves interaction with a porous surface

In that sense, the efficiency of a sound absorber is a balance between a small amount of sound reflection and large amount of sound dissipation as illustrated in Figure 1. 17.

There are three main classifications of absorbers: discrete, porous, and resonant (which include membranes and Helmholtz resonators, also known as perforated absorber). Discrete absorbers can literally be anything: panel, wall, person, bookshelf, etc.[202]

Porous absorbers are the most common and include natural fibers (e.g., cotton), mineral fibers (e.g., glass fiber), foams, carpets, and so on.[203] When the sound waves strike the surface of a porous absorber (such as an open cells foam), the air flows through the material forcing the cell walls to stretch, bend and buckle. These frictional forces convert the sound energy into heat.[202] According to this view, the closed cells foams would not absorb sound well. However, others mechanisms explain the sound absorption of these materials.

The membrane absorbers utilize the resonant properties of a flexible membrane to absorb sound. An example of membrane absorbers are the wood panels mounted in front of the rigid back where air columns inside vibrate responding to incident sound waves. The friction between the air and the walls results in absorption of sound energy.[203] In turn, Helmholtz absorbers consists in enclosed volume with a relatively small aperture. The most common examples of Helmholtz resonators are bottles and jugs. The performance of membrane absorbers and Helmholtz resonators is directly related with the dimensions of their cavities as well as the stiffness of their walls.[203] In fact, a membrane absorbers can be converted into a Helmholtz resonator by cutting or drilling openings in the face of the membrane.

The similarity between the cellular structures of the foams (Figure 1. 6) with the absorbers represented in Figure 1. 18 are evident.

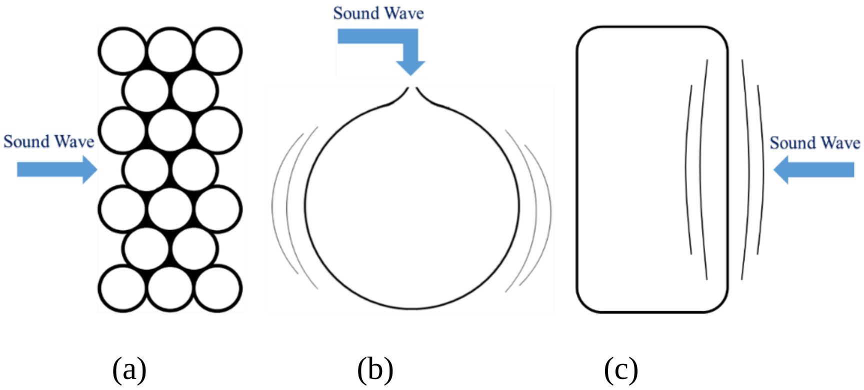


Figure 1. 18 - Porous absorber (a), Helmholtz absorber (b) and membrane absorber (c)

For instance an open cell foam can act as a porous absorber, a closed cell foam can act as a membrane absorber and an open/closed cell foam can act as a Helmholtz/perforated membrane absorber. Therefore it is useful to know the relationship between the mechanical properties and porous structure of a foam with their sound absorption capability. There have been many studies attempting to predict them, including studies about airflow resistivity, porosity, elastic constants, pore geometry and so on.[139,202,204]

An easy way to design a PUF with enhanced sound performance is by tuning its formulation in order to achieve the appropriate cellular structure. Whilst many studies have reported in the literature in connection with sound absorbing properties of flexible PUFs, far less attention has been paid to that of rigid PUFs. Studies have however indicated the potential application of liquefied coffee grounds derived foams as sound absorbing materials due to their potential for damping of vibrations.[97] Nevertheless, further studies still need to be carried out such as the partial addition of different polyols to improve the sound absorption properties of PUFs derived from renewable resources. This challenge will be addressed in Chapter 6.

1.6. Recover polyols from PUs waste materials

Due to their variety of applications, the production of PUs has increased in the past decades, leading to an increase of PU wastes, as well as an increase of the concern about its disposal.[205]

Various approaches have been developed in an effort to reclaim the waste foam. PUFs wastes generated in production or recovered after use can be recycled by shredding and mixing with a PU binder to make carpet underlay. In addition, there are others methods, such as landfill and incineration, but neither are acceptable because long-range ecological goals dictate zero pollution as well as conservation of raw materials.[206]

Despite landfill and incineration, the disposal technology for PUs wastes can be achieved by its recycling [207] since due to ecological and environment problems, landfill and incineration are not valid options. In that sense, PUs wastes must be effectively recycled, which is not only a requirement of preventing pollution and environment protection, but is also a need for its production cost reduction and for the material utilization efficiency.

There are two major categories for the recycling of PUs: physical recycling and chemical recycling. In physical recycling the PU scraps are directly reused without chemical treatment, while the chemical recycling follows the degradation principle. So the PU wastes are gradually depolymerize into other oligomer and even small molecules.[207]

Years of research and development lead to many thermo-chemical methods for the recycling of PUs, such as hydrolysis, glycolysis, alcoholysis, aminolysis, among others.[208]

Hydrolysis of PUs is based on the use of overheated steam, which hydrolyzes urethane bonds under the formation of polyols and amines.[209] After separation and purification they can be reused as raw materials for PUs production. However, the separation and purification of hydrolytic products of PUs are insofar costly, making the process not economically feasible.

Aminolysis of PUs is based on breaking urethane bonds with amines (e.g. with dibutylamine or ethanolamine) giving rise to polyols and disubstituted ureas. The final products are oligomeric ureas and amines.[210]

Regarding to alcoholysis, the substitution of one hydrogen atom of water by an aliphatic group leads to alcohols. The reaction is performed in a similar way as the hydrolysis. It require high temperature under pressure. It was developed hoping a more easily separation of the amines from the polyol methanol mixture, but the separation is nearly as difficult as the hydrolysis products and additionally, methanol have to be evaporated. Numerous patents with respect to alcoholysis are available but none of the process described entered into larger scale application.[211]

The most common method, which is currently used in industry, is the glycolysis which uses higher boiling glycols as decomposition reagents.[212] A common drawback of PU glycolysis processes is high energy demands and long reaction times, which significantly restricts their utilization in industry. [213]

All these methods have advantages and disadvantages, but the glycolysis is the most commonly used at the industrial scale.

However a new route or recycling PU scraps is emerging by converting it into a liquid, using a cleavage agents (dicarboxylic acids). The cleavage agent reacts with the carbamic group bond of the PU network, which will gradually depolymerize into small molecules, being carbon dioxide and water the reaction sub products.

Many dicarboxylic acids can be used in the acidolysis of PUs scraps, such as oxalic acid, malonic acid, succinic acid, or adipic acid. Also, they can be used singly or as a mixture of at least two and its type and quantity can be adjust/optimized to the characteristics required for the recovered polyol.

Others additives can be additionally used, such as catalysts, UV stabilizers, surfactants, plasticizers, emulsifiers, among others.

The temperature and reaction time are an important parameters because it must be maintained within a specific range in order to the obtained polyol present suitable characteristics to be used in the PU production. Low temperatures and reaction times thus a final product with higher acid value, lower hydroxyl value, higher molecular weight and higher viscosity. Higher temperatures and reaction times thus a recovered polyol with lower acid value, higher hydroxyl value, lower molecular weight and lower viscosity, but can darken the color of the polyol. In that sense, the reaction temperature and reaction time can be adjust/optimized to the characteristics required for the recovered polyol. This issue will be addressed in Chapter 7.

2. Evaluation of the influence of CG composition on the properties of PUFs

This chapter was presented as oral communication (N. V. Gama, R. Silva, C. S. R. Freire, C. Pascoal Neto, A. Barros-Timmons, A. Ferreira, "Rigid polyurethane foams from unrefined crude glycerol – study of crude glycerol composition"), at the Mat´Cell conference, in Aveiro, in 2015. Also was published in the Journal of Cellular Plastics (Nuno V. Gama, Belinda Soares, Carmen S. R. Freire, Rui Silva, Artur Ferreira, Ana Barros-Timmons; Effect of unrefined crude glycerol composition on polyurethane foams properties, Journal of Cellular Plastics, https://doi.org/10.1177/0021955X17732304). Finally, part of this chapter was submitted for patent application (A. Ferreira, N. V. Gama, B. Soares, C. S. R. Freire, A. Barros-Timmons, C. Pascoal Neto, R. Silva, I. Brandão, "Method for production of rigid polyurethane foams using unrefined crude glycerol", National Patent - 107711 E, *2014/06/12)*

2.1. Abstract

The aim of this study is to evaluate the possibility of using unrefined CG, a byproduct of the biodiesel industry, in the production of PUFs. In order to assess the suitability of this raw material for the production of PUFs, two samples of CG with different compositions in glycerol, fatty acids and methyl esters were used directly, without any pre-treatment or purification. Additionally, one of these samples was also submitted to a pre-treatment step in order to evaluate the advantage of purifying the raw material and, for comparison, pure glycerol was also used to prepare PFUs. Both chemical and structural characterizations of the produced foams, as well as the thermomechanical properties determined, showed that unrefined CG is a suitable ecopolyol for the production of PUFs. Although the presence of fatty acids and esters affects their mechanical performance this issue can be explored to tune the properties of the ensuing PUFs. Furthermore, the evaluation of the impact of using unrefined CG on the sustainability of PUFs production yielded promising results.

Keywords: Crude glycerol; unrefined crude glycerol; polyurethane foams; chemical composition; foaming process; sustainability evaluation

2.2. Introduction

To address the growing constraints associated with the use of fossil raw materials, many efforts have been made to find alternatives derived from renewable resources for both materials and energy. In this context, the interest in the biodiesel fuel technology has received much attention. Yet, this technology generates CG as the main by-product, with circa 1 kg of CG being generated per 10 kg of biodiesel produced.[214,215] Therefore, concerns about its disposal are being raised.

Typically, CG contains various impurities, including fatty acids, alkoxide salts, inorganic salts, "matter organic, non-glycerol" (MONG), water and unreacted methanol. Whilst high purity glycerol has relevant market value, particularly in the cosmetic and pharmaceutical industries.[214,215] Additionally, the composition of CG varies depending on the feedstock used, which implies different and adjustable processes which limits scaling up. Nevertheless, commercialization of renewable resources based chemicals, such as CG is gathering speed and major companies such as Dow and Solvay being already actively involved.[216] The use of CG in the production of PUFs can be as well attractive.

PUs are versatile engineering materials which find a wide range of applications because their properties can be tailored by the type and composition of their components.[96] Like other polymers, PUs rely on petroleum feedstocks and the increasing concern over the environmental impact and scarcity of petroleum, has motivated the development of PUs from bio-based and renewable raw materials.[47] For example, oxypropylated lignin,[217] oxypropylated cork,[64] starch,[218] soybean,[219] sugar beet pulp[63] and date seeds[72] have been used to replace conventional polyols in the synthesis of PUFs and the ensuing foams had comparable foaming kinetics, density, cellular morphology, and thermal conductivity to those obtained from petroleum. However, the processes used to obtain polyols from this type of resources generally require high temperature or high pressure. Other, more environmentally friendly processes have been developed at atmospheric pressure which include the use of liquefied cork and liquefied coffee grounds wastes, for example.[97,220] CG being a polyol, has also been studied as an alternative raw material for the production of PUFs[155] and a couple of processes regarding the treatment of CG and subsequent use in the production of PUFs have been patented.[152,154] As an alternative, our group has patented the direct use of CG in the production of PUFs.[52] However, in view of the variable composition of CG, further studies are required. Li *et al.* have reported the preparation of biopolyols, from CG, via a one-pot thermochemical process and subsequently used them in the production of PUFs. They have concluded that the presence of branched fatty acid ester chains in biopolyols helps reducing the degree of microphase separation and stabilize the bubbles during the foaming process.[157] With this in mind and together with our interest in minimizing CG refinement and/or modifications aiming at more environmentally friendly and cheaper raw materials, in the present study the impact of CG composition on the properties of the ensuing PUFs is evaluated. Foams were prepared using the same base formulation and polyols with different chemical characteristics, and their chemical and structural characteristics, mechanical and thermal properties measured. Finally, a brief evaluation of the use of these ecopolyols on the sustainability of PUFs production was carried out.

2.3. Experimental

2.3.1. Materials

PUFs were produced via the reaction of CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. CG samples (CGA and CGB) were supplied by Bioportdiesel and used as polyol. CGA was also submitted to an acid pre-treatment step affording sample CGT. Glycerol (GLY) with 99.5% purity, was supplied by Sigma-Aldrich. The polymeric isocyanate Voranate M229 MDI (methylene diphenyl diisocyanate) was supplied by Dow Chemicals. Tegostab B8404, was used as surfactant and supplied by Evonik. Polycat 34, was used as catalyst and supplied by Air Products. Distilled water was used as blowing agent.

2.3.2. Pre-treatment of crude glycerol

The pre-treatment of CG was carried out in a computer controlled 70 L stainless steel pilot plant reactor at 150 ºC, using 4% (w/w) of sulfuric acid during 60 min. The product was dissolved in ethanol and neutralized with a NaOH solution (0.5M). Upon neutralization, the product was filtered to remove the salts and soaps formed and finally, ethanol was distilled off to afford CGT.

2.3.3. Characterization of glycerol

The determination of water content, acid value (AV) and hydroxyl number (OH_{number}) of the polyols samples has been described in Chapter 1. For the determination of ash content, 1 g of polyols was heated at 800 ºC for 6h and the residual mass was divided by the initial mass. The glycerol, fatty acids and methyl esters relative composition was determined by GC-MS, using a Trace Gas Chromatograph 2000 Series equipped with a Thermo Scientific DSQ II mass spectrometer, using helium as carrier gas (35 cm s^{-1}) and equipped with a DB-1 J&W capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The chromatographic conditions were as follows: initial temperature: 80 °C for 5 min; temperature rate of 4 °C min^{-1} up to 260 °C and 2 °C min^{-1} till the final temperature of 285 °C; maintained at 285 °C for 10 min; injector temperature: 250 °C; transfer-line temperature: 290 °C; split ratio: 1:50. The MS was operated in electron impact mode with electron impact energy of 70 eV and data collected at a rate of 1 scan s^{-1} over a range of mz^{-1} 33–700. The ion source was maintained at 250 °C.

Table 2. 1 - Polyol samples identification and chemical characterization

		CGA	CGB	CGT	GLY
M_n		154.4	163.8	97.8	92.1
H_2O		1.6	0.4	1.6	0.1
AV		23.1	59.9	0.1	1.6
OH_{number}		399.0	323.4	497.7	520.9
Relative chemical composition (%)	Glycerol	84.1	60.1	98.2	100
	Fatty acids	10.0	21.3	0.6	0
	Methyl esters	5.9	18.6	1.2	0
Ashes		2.3	1.7	0.2	0

2.3.4. Production of PUFs

In general, the PUFs formulations used were established based on our previous experience in the production of PUFs.[52] Each polyol and the corresponding amounts of catalyst (3 parts per 100 parts of polyol w/w), surfactant (4 parts per 100 parts of polyol w/w) and blowing agent (6 parts per 100 parts of polyol w/w), were placed in a 100 mL polypropylene cup and homogenized using an mechanical stirrer for *ca.* 10 seconds at 700 rpm. Note that the amounts of water present in the polyols were subtracted from the amounts of blowing agent used. Next, the appropriate amount of isocyanate to obtain a $R_{NCO/OH}$=1.10 (ratio between NCO groups of isocyanate and OH groups) was added and the mixture homogenized again. The $R_{NCO/OH}$ used in the PUFs production were determined using Eq. 11.

$$R_{NCO/OH} = (m_{iso} \times \%_{NCO}/M_{NCO})/(m_{polyol} \times (OH_{number} + AV)/M_{KOH} + (m_{H2O} + m_{BA}) \times Eq_{H_2O})$$

(Eq. 11)

Where $R_{NCO/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH moles of polyol and water, m_{iso} is the mass (g) of isocyanate, $\%_{NCO}$ is the quantity of NCO groups in the isocyanate (31.1%) and M_{NCO} is the molecular weight of NCO group. m_{polyol} is the mass (g) of each polyol, OH_{number} and AV are the hydroxyl number and the acid value of each polyol respectively (mg_{KOH} g^{-1}). M_{KOH} is the molecular weight of KOH. m_{H2O} is the mass of water present in the polyol while m_{BA} is the mass of blowing agent (water) added. Finally, Eq_{H2O} is the equivalent of OH groups present in the water. The foams were obtained by free expansion in the cup mold at room temperature.

Table 2. 2 - PUFs formulations

Sample	Polyol	Catalyst (PHP)	Isocyanate (PHP)	Surfactant (PHP)	Blowing agent (PHP)
PUF-CGA	100	3	220	4	5
PUF-CGB	100	3	200	4	6
PUF-CGT	100	3	250	4	5
PUF-GLY	100	3	230	4	6

2.3.5. Characterization of PUFs

Each foam was characterized by Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), density, thermal conductivity measurements, compressive tests, Dynamic Mechanical Analyses (DMA) and thermogravimetric analysis (TGA) according to procedures and conditions described in Chapter 1. ^{13}C solid-state Cross Polarization—Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C CPMAS NMR) spectra were recorded on a

Bruker Avance 400 spectrometer. Acquisition parameters were as follows: ca 7000 scans with a 90 proton pulse, a crosspolarization contact time of 1 ms and a recovery delay of 2.5 s. The porosity of the samples was determined by nitrogen adsorption using the Gemini V equipment (Micromerities) at room temperature. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method.[36] The pores volume and their diameters were calculated according to the model developed by Barret, Joyner e Halenda (BJH).[37]

2.4. Results and discusion

The main objective of this work was to assess the viability of using unrefined CG and evaluate the effect of impurities on the production of PUFs. To achieve that four different samples have been considered: two untreated CG samples (CGA and CGB) with different chemical compositions, pure glycerol (GLY) and a fourth sample which consisted in CGA that was submitted to an acid pre-treatment step (CGT). As a starting point, the polyols were submitted to a detailed chemical characterization.

2.4.1. Characterization of the polyols

GC-MS was used to determine the relative composition of CGA, CGB, CGT and GLY. The MS spectra collected are shown in Figure 2. 1 and the detailed polyols composition presented in Table 2. 3. The M_n, water content, AV and OH_{number} of each polyol were determined and the data are summarized in Table 2. 1.

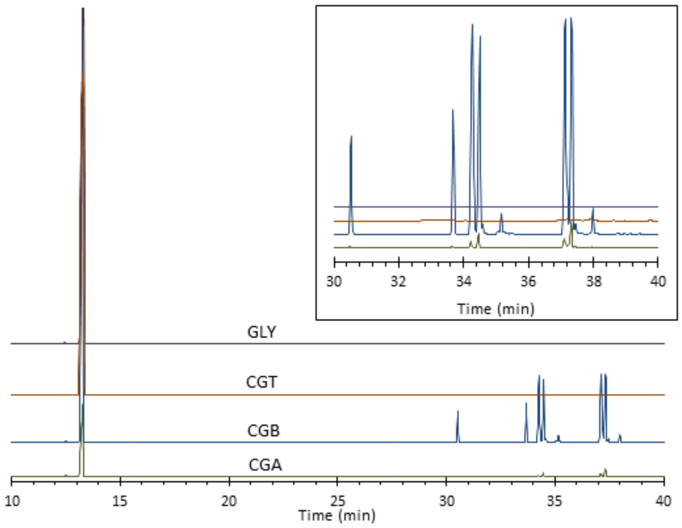


Figure 2. 1 - GC-MS of CGA (a), CGB (b) and CGT (c) GLY

From Figure 2. 1 it is clear that the composition of CG samples A and B is significantly different with CGB being richer in fatty acids and esters. Furthermore, it is also evident that the acid pre-treatment yielded a sample that is free of fatty acids or esters as it can be seen in Table 2. 3.

Table 2. 3 - Detailed relative composition of polyols tested

Compound	CGA	CGB	CGT	GLY
Glycerol	84.1%	60.1%	98.2%	100.0%
Palmitic acid methyl ester	0.5%	3.3%	0.1%	0.0%
Palmitic acid	0.5%	4.1%	0.1%	0.0%
Linolenic acid methyl ester	1.9%	9.1%	0.6%	0.0%
Oleic acid methyl ester	3.5%	6.3%	0.5%	0.0%
Linolenic acid	3.1%	9.8%	0.2%	0.0%
Oleic acid	6.5%	7.4%	0.3%	0.0%

These results highlight significant differences between these samples, which are critical for the PUFs production. As expected the molecular weight of the samples is directly related to the percentage of fatty acids and esters with unpurified samples (CGA and CGB) having higher M_n than CGT or GLY. In turn, the *AV* is directly proportional to the presence of alkyl esters and acids which has been ascribed to the presence of the fatty acids in the polyols.[221] Conversely, the

OH_{number} of polyols is lower for samples CGA and CGB as the degree of hydrolysis is lower than that of the acid treated sample, and of GLY. Notice should be made that the OH_{number} value determined for GLY is much lower than those commonly reported in the literature. This is due to the analytical method used. In this study, for adequate comparison with the remaining samples, the procedure followed consists in an adaptation of the ASTM D4274-05 standard. Namely, the equivalent point of the titration was determined using a pH meter instead of the phenolphthalein method.

Having characterized the polyols, the effect of their chemical composition on PUFs properties was investigated. The reaction was monitored by FTIR spectroscopy and the ensuing products characterized by a variety of techniques trying to establish correlations between the chemical composition of the CG samples and the properties of PUFs to assess the need for an extra purification step of the unrefined samples.

2.4.2. Monitoring of the reaction

FTIR analysis was used to monitor the formation of the urethane linkages, as a result of the reaction between the NCO groups of the isocyanate and the OH groups of the polyols, as well as to monitor the extent of this reaction. All normalized FTIR spectra (see Figure 2. 2) presented very similar profiles and do not reveal differences in the urethane arrangements and/or hydrogen bonding network.

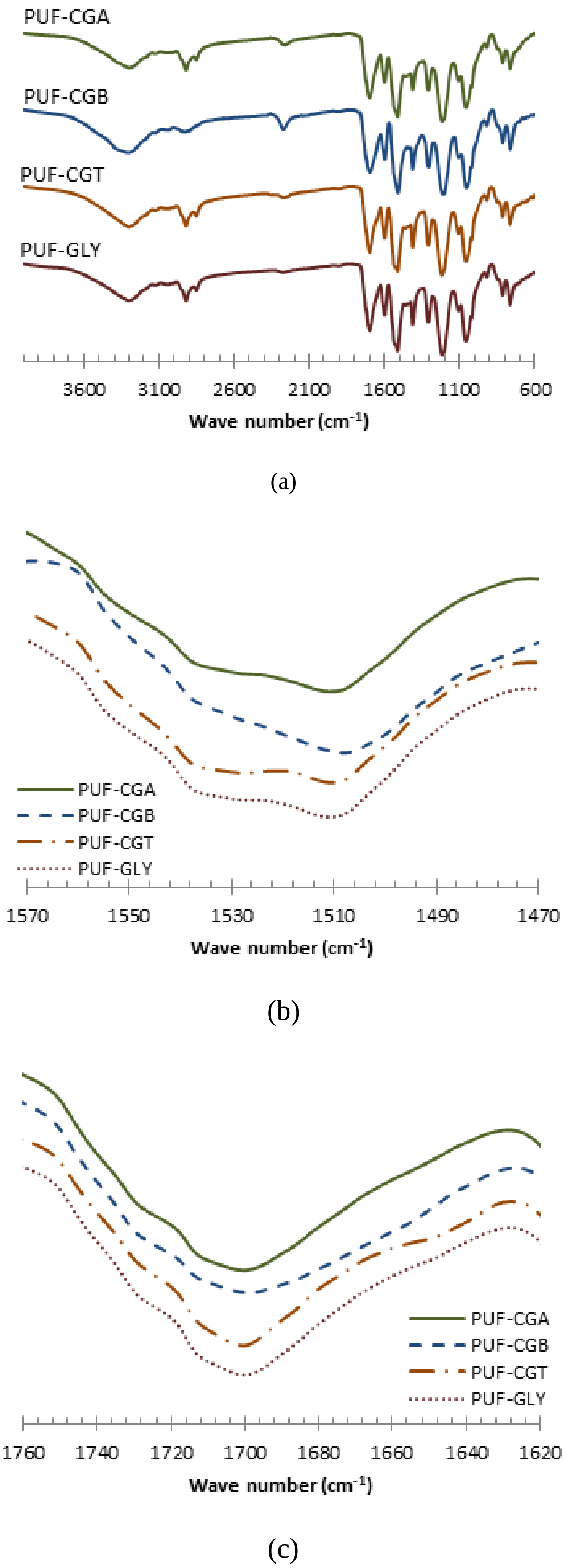


Figure 2. 2 - Normalized FTIR spectra of PUFs prepared using CGA, CGB, CGT and GLY (a), expansion of the spectra in the 1570-1470 cm-1 range (b) and in the 1760-1620 cm-1 range (c)

All normalized FTIR spectra are presented in Figure 2. 2 present very similar profiles. The band in the 3200–3450 cm^{-1} region is attributed to the non-bonded stretching vibrations of O-H groups and symmetric and asymmetric stretching vibrations of the N-H of the urethane and of urea groups (resulting from the reaction between water and isocyanate groups). The bands between 2950 and 2850 cm^{-1} correspond to the asymmetric and symmetric C-H stretching vibrations respectively. The peak at 1710 cm^{-1} is ascribed to the stretching vibrations of the C=O. The nearly overlapped bands between 1540 and 1517 cm^{-1} are associated with the free N-H absorption and the N-H groups which are hydrogen-bonded with carbonyl groups, respectively. Finally, notice should be made to the peak around 2270 cm^{-1}, typical of residual NCO groups. This is attributed to the fact a 10% excess of isocyanate over the polyols was used (i.e. $R_{NCO/OH}$=1.1) as well as with the different reactivity of some of the OH groups of polyol. In fact, it is known that isocyanate reacts faster with primary OH groups than with secondary OH groups.[222] Moreover, the presence of the hydrophobic alkyl chains attached to CGA and CGB may hinder access of the OH groups to the isocyanate ones. Indeed, the band at 2270 cm^{-1} is particularly noticeable for sample CGB. Nevertheless, the presence of methanol cannot be negligible, because it can react with the isocyanate groups and/or the alkyl esters. As the two regions highlighted in Figure 2. 2 b) and c) can bring insight into the effect that chemical composition of polyols can have on the hydrogen bonds network of PUFs and thus on their properties, they have been expanded and analyzed in more detail. As it can be observed neither region suggests any major difference. In fact, the absorption of the carbonyls at 1710 cm^{-1} indicates strong H-bonding in all the PUFs. Similarly, in the N-H region the band at 1517 cm^{-1} is slightly more intense for all the sample confirming the presence of H-bonding. Additionally, it should be remarked that the band at 1640 cm^{-1} ascribed to H-bonded urea groups is also present in the spectra of all the samples with similar intensity. This inspection suggests that in all cases reasonably ordered urethane segments are formed and that microphase separation associated with the alkyl moieties does not seem to be present. In turn, the band at 1640 cm^{-1} clearly indicates the presence of ordered hard domains.[223] Yet, microphase separation was not confirmed by DMA, probably as a result of the small molar mass of the soft domains and the high level of crosslinking.

To further evaluate the effect of the chemical composition of the polyol on the ensuing foams, solid state ^{13}C magic angle spinning (MAS) NMR was used and the spectra collected are illustrated in Figure 2. 3.

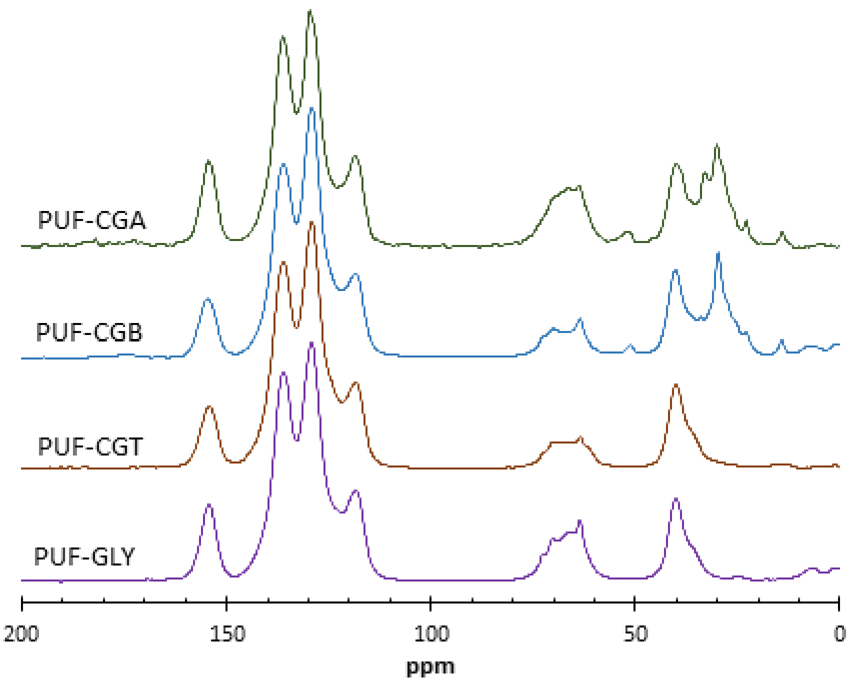


Figure 2. 3 - ^{13}C CPMAS NMR spectra of PUFs prepared using CGA, CGB, CGT and GLY

The peak at 30 ppm in the spectra of PUF-CGA and PUF-CGB was attributed to the methylene groups of the alkyl chains, though in the case of PUF-CGA a shoulder at lower field could be identified. The remaining peaks are similar for all the samples and are typical of PUFs.[224]

2.4.3. Morphology

As the use of different polyols can have a major impact on the foaming mechanism and thus on the properties of the resulting materials, the morphology of PUFs was analyzed by SEM and the images of the cross-section surface are shown in Figure 2. 4.

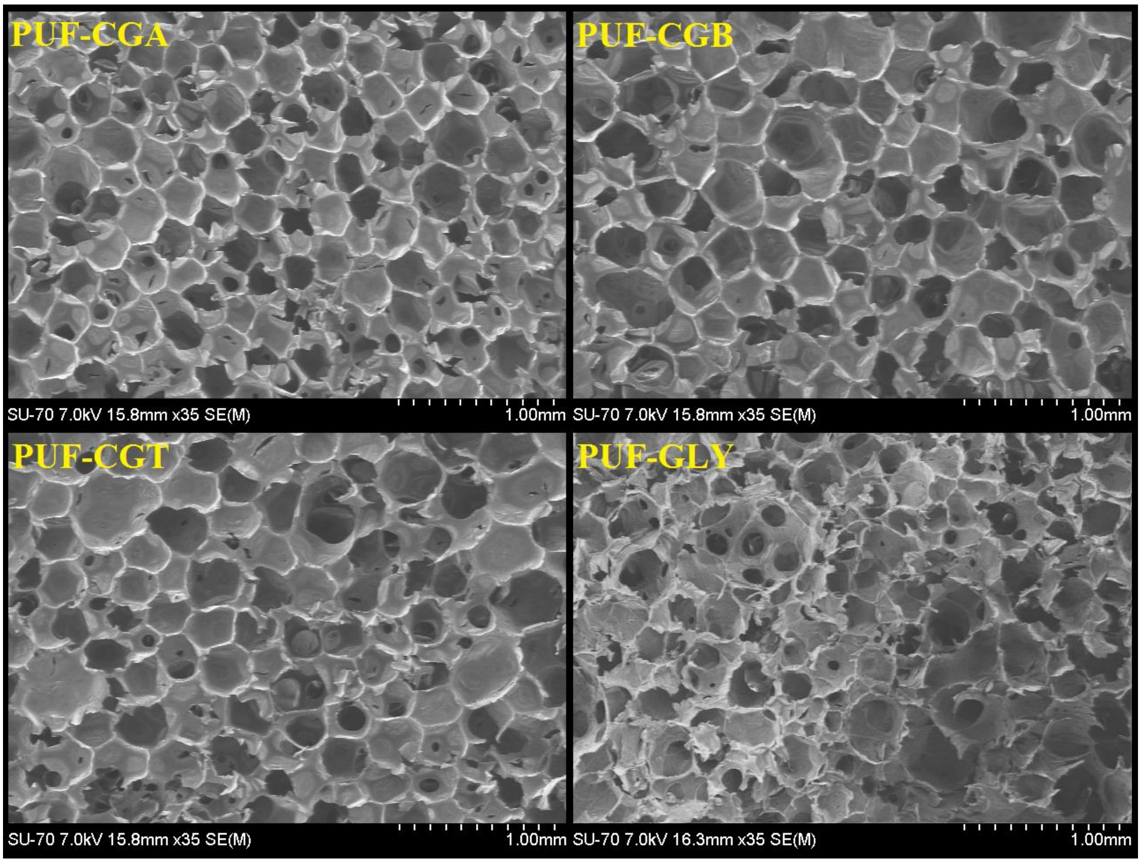


Figure 2. 4 - SEM images of PUF-CGA, PUF-CGB, PUF-CGT and PUF-GLY at 35x magnification

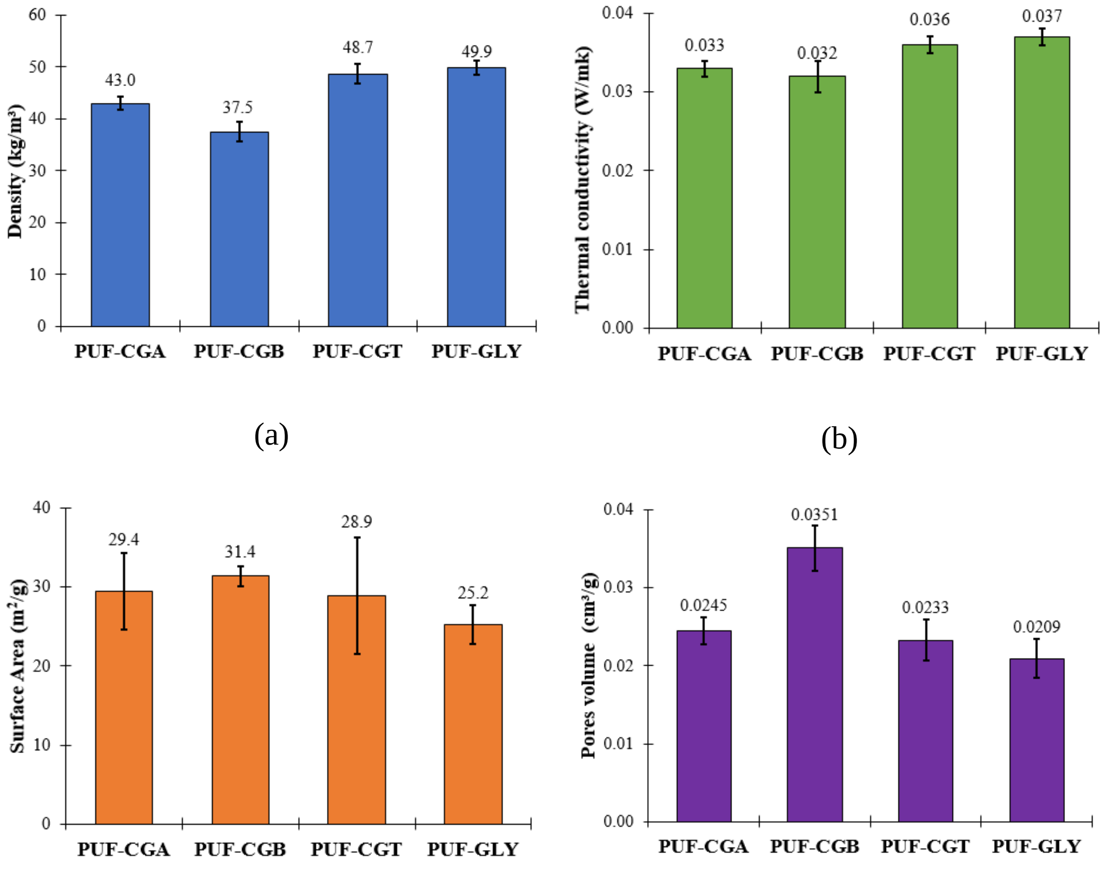
The typical cellular structure of PUFs is clearly observed for all foams derived from CG but when pure GLY was used the cellular structure, though present, is different showing extensive cell rupture. These results indicate that the chemical composition of the polyol seems to affect the foaming process. However, it is not possible to clearly pinpoint a specific effect. During mixing air bubbles are introduced in the reaction mixture which act as nucleation sites for the blowing gas generated from the reaction between isocyanate and the blowing agent. These bubbles grow yielding a closely packed network of bubbles responsible for the typical cellular structure of PUFs.[218] Thus, the morphology of PUFs depends on the quantity of gas released in the course of the polymerization, the density of crosslinking of the polymer matrix formed and the surface tension, among others. In view of the complexity of the foaming process, the morphologies of the foams richer in glycerol was first compared in an attempt to correlate the chemical characteristics of the polyols used with the ensuing cellular structures.

Considering that the main difference observed form SEM images is between samples PUF-CGT and PUF-GLY, whose polyols consist essentially in glycerol, the effect of OH_{number}, AV, water content and the presence of residual chemicals was evaluated step by step. Between CGT and GLY the difference in OH_{number} is 23 which not so dramatic when compared with the difference in OH_{number} of these polyols and those of untreated CG which is above 100. Hence, the crosslinking density and rigidity of the polymeric networks formed should be similar. As regards the difference in AV (1.5), one could be tempted to consider the difference relevant. Yet, when compared to the difference in AV values of these polyols and those of unrefined CG (> 20), this cannot justify the difference in morphology observed for the PUFs derived from CGT and GLY.

As regards the morphology of PUF-CGA and PUF-CGB when compared to the other foams the differences, though not very striking, may be attributed to the presence of alkyl acids and esters. In fact, the alkyl chains of these moieties are thought to make the polymer network more flexible allowing a more regular expansion without major deformation of the cell wall. Additionally, it is also possible that the free fatty acids may act as co-surfactants helping the stabilization of the bubbles during foaming. Indeed, as it will be discussed later, the presence of residual free fatty acids in CGT is thought to be associated with the differences detected in the morphology of PUF-CGT when compared with that of PUF-GLY. This indication is more evident when the porosity results, presented next, are considered.

2.4.4. Density and porosity

In order to further assess the effect of the chemical composition on the morphology of the ensuing foams BET and density measurements were carried out. It is a general rule that the density of foams depends on the quantity of gas released during the blowing agent/isocyanate reaction and on the quantity and nature of the surfactant. Considering that the same base formulation was used for all the samples, it would be intuitive to associate higher densities with higher OH_{number}, as well as smaller pore volumes. Indeed, generally that was the case as illustrated in Figure 2. 5. However, the trend observed is not straightforward which confirms that the foaming process is complex and cannot be just explained by differences in OH_{number} alone. Indeed, although the presence of fatty acids and esters in CGA and CGB is associated with smaller OH_{number} values, the differences between the density of PUF-CGA and PUF-CGT or PUF-GLY suggest that the fatty acids are in fact involved in the bubbles' stabilization and the foaming process in general. These results are in agreement with those obtained for porosity measurements confirming that the area and volume of the pores of PUFs is higher when polyols containing alkyl acids and/or esters are used.



(a) (b)

(c) (d)

Figure 2. 5 - Density (a), Thermal conductivity (b), Surface area (c) and Pores volume (d) of foams

2.4.5. Thermal conductivity

The effect of the chemical composition of CG was also evaluated on the thermal conductivity (*k*) of the ensuing foams and the data obtained are plotted in Figure 2. 5. As it can be observed the differences are small. In fact they are within the range of the error, with lower *k* values obtained for the foams with lower densities. The *k* values obtained for PUF-CGA and PUF-CGB (*ca* 0.033 W m^{-1} k^{-1}) are equivalent to those of commercially available rigid foams hence, they are suitable for thermal insulation applications.

2.4.6. Mechanical properties

Compressive tests were performed to study the mechanical properties of PUFs and assess the effect of the chemical composition of the CG used as raw material. Figure 2. 6 illustrates the typical compressive stress-strain plots of PUFs prepared and in Table 2. 4 the values of Young's modulus, toughness and compressive stress are summarized. The results presented are averages of 10 specimen measured for each type of PUF.

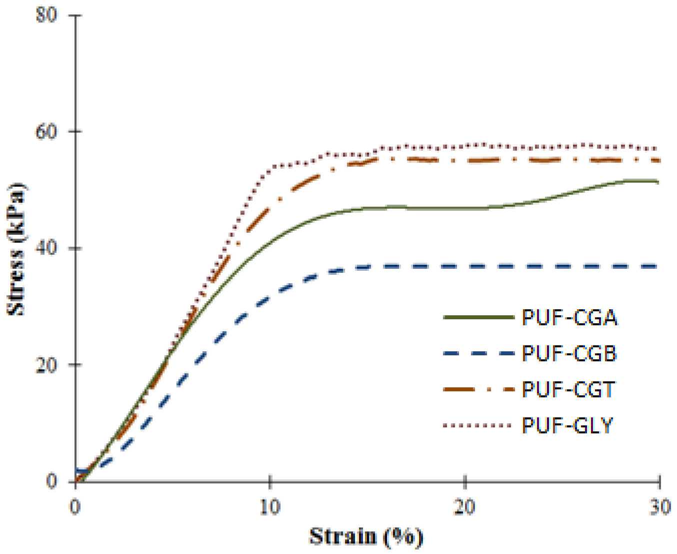


Figure 2. 6 - Compressive stress-strain curves of PUFs

As it can be observed, in the linear region, associated with the elastic response of the samples, foams PUF-GLY, PUF-CGT and PUF-CGA have a similar response up to 0.05 strain.

Yet, for PUF-CGA the plastic deformation starts at lower values of stress and it seems to be followed by densification or polymer hardening beyond 20% strain. Distinctively, PUF-CGB presents a lower slope in the linear region which is followed by the plastic region and no sign of densification is observed.[225] These observations are reflected in the values determined for Young's modulus, compressive stress and toughness (Table 2. 4). The differences can be related to the crosslinking density which in turn is related to the OH_{number}. However, as previously discussed for the density and the morphology of the cells, the results obtained cannot be exclusively attributed to the number of OH groups available to react with the isocyanate and/or their reactivity. Besides the crosslinking density, the size and shape of the cells can also play a significant role which is related to the effect that the alkyl acids and esters may have in the foaming process. Furthermore, the presence of flexible segments of the alkyl acids and esters alters the mechanical performance of the foams. In fact, a higher percentage of these chemical species in CGB afforded foams with lower densities and much weaker mechanical properties. The role of these flexible moieties was further confirmed when the effect of porosity was removed which can be done by calculating and analyzing the specific Young's modulus, toughness and compressive stress.

Table 2. 4 - Young's modulus, compressive stress (σ10%) and toughness normalized for density and corresponding specific values

PUF	Young's modulus (kPa)	Toughness (J m^{-3})	Compressive stress 10% (kPa)	Specific Young modulus (m^2 s^{-2})	Specific toughness (m^2 s^{-2})	Specific compressive stress (m^2 s^{-2})
PUF-CGA	617.7 ± 12	15313 ± 2669	44.9 ± 3	14377	356416	1045
PUF-CGB	539.9 ± 19	8313 ± 1209	36.6 ± 2	14397	221621	975
PUF-CGT	680.1 ± 19	19300 ± 2352	50.5 ± 4	13977	396653	1038
PUF-GLY	699.5 ± 26	20800 ± 1752	53.3 ± 3	13753	417043	1068

2.4.7. Dynamic mechanical analysis

DMA measurements were carried out in order to get complementary information about the mechanical response of the PUFs to further assess the effect of the chemical composition of the polyols used on their thermal and the viscoelastic properties. See Figure 2. 7.

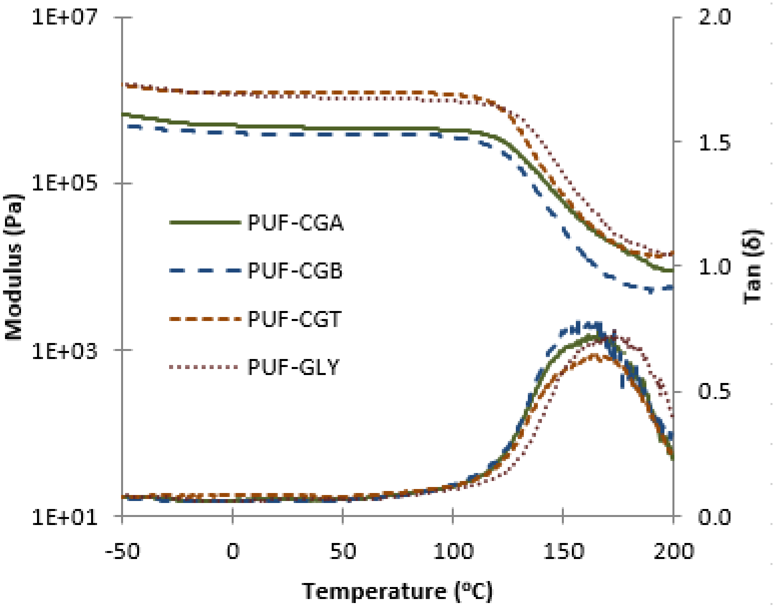


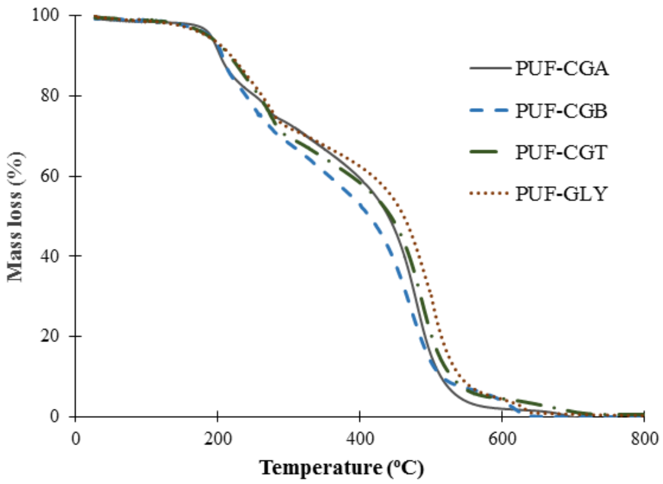
Figure 2. 7 - Temperature dependence of the storage modulus and tan (δ) of PUFs prepared using CGA, CGB, CGT and GLY

Below the glass transition temperature, PUF-GLY and PUF-CGT have similar storage modulus around 1.1x10^6 Pa. Interestingly, in this type of dynamic mode of analyses, the behavior of PUF-CGA and PUF-CGB is much more similar then that observed for the stress-strain tests, and both materials have a storage modulus nearly one order of magnitude lower (*ca* 4x10^5 Pa) than the other foams. This difference cannot be attributed to distortion of the cellular structure as these foams have a better cellular structure than PUF-GLY and PUF-CGT. Hence, these differences may be associated with the plasticizing effect that fatty acids and esters have on the viscoelastic response of the polymeric matrix, together with the lower crosslinking density resulting from the lower OH_{number} of the polyols used. This is confirmed by the T_g of PUFs, measured at the top of the tan (δ) which were 166.1 ºC, 157.7 ºC, 168.3 ºC and 173.0 ºC for samples prepared using

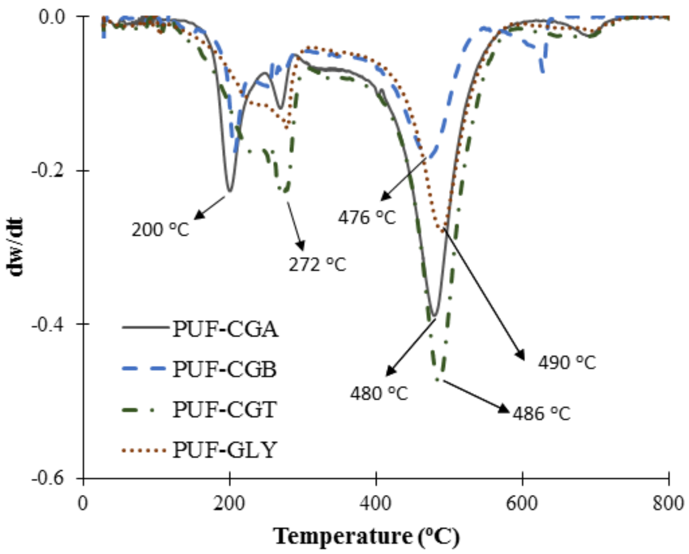
CGA, CGB, CGT and GLY respectively. This trend is in agreement with the behavior reported by T. W. Pechar *et al.* for soybean-based PUFs who obtained higher T_g values for samples prepared using polyols with higher OH_{number}.[226] However, in the present study, the plasticizing effect of unbound alkyl acids should not be ignored. Considering that samples porosity affects the viscoelastic response of PUFs, the values of T_g were also determined for powdered samples using the material pocket accessory of the DMA instrument. The values obtained were 153.7 ºC for PUF-CGA, 141.6 ºC for PUF-CGB, 169.6 for PUF-CGT and 173.7 ºC for PUF- GLY, confirming that the presence of alkyl acids and esters reduces the T_g of the ensuing foams.

2.4.8. Thermogravimetric analysis

The thermal degradation of the four PUF samples was investigated by TGA and Figure 2. 8 displays the corresponding TGA curves and respective derivatives.



(a)



(b)

Figure 2. 8 - Thermal degradation (a) and dw/dt (b) of PUFs

As expected the decomposition profiles observed are typical of PUFs which are characterized by two main decompositions steps: one around 200 ºC, related to the thermal decomposition of the hard segments (e.g. urethane groups) and a second, around 460 ºC related to the soft segments.[159,227,228] Considering the presence of fatty acids and esters of PUFs derived from unrefined CG, their decomposition occurs during the first step.[157] Although Figure 2. 8 (a) only reveals small differences in the second decomposition step associated with the soft segments, when the derivatives are considered, (Figure 2. 8 (b)) it becomes clear that there are also differences in the first decomposition step. In fact, the relative proportion of the areas of the two peaks around 200 and 272 ºC in the case of PUF-CGA and PUF-CGB is distinct from that observed for PUFs derived from GLY and CGT. As regards the decomposition of the soft segments, the temperature at which their maximum rate of decomposition occurs is also directly related to the chemical composition of the polyol used with values increasing as the percentage of fatty acids and esters decreases, i.e. 476 ºC, 480 ºC, 486 ºC and 490 ºC for PUF-CGB, PUF-CGA, PUF-CGT and PUF-GLY, respectively. Despite of a possible heterogeneity of the foams, these differences are associated with the crosslinking density, type and structure of the polyols.[190] Nevertheless, all the foams were thermally stable up to 180 ºC which is within the range found for other PUFs obtained from renewable resources.[50]

2.4.9. Brief sustainability evaluation

Based on green chemistry principles three sustainability indicators have been selected to briefly evaluate the impact of using polyols of different sources towards sustainability of foam production. For that purpose a simple calculation methodology, inspired in multicriteria based evaluation tools was used.[229,230] Besides the four types of polyols considered in the present study, a conventional polyol commonly used in PUFs production was also considered for this evaluation. The three sustainability indicators considered were *(i)* environmental indicators: feedstock renewability, energy intensity, waste generation, CO_2 balance; *(ii)* economic indicators: yield, feedstock price, process costs; *(iii)* social indicators: process conditions, chemicals safety, innovation potential. Next, the best performance for each indicator was classified with 1.0, the worst with 0.0, and intermediate performances with 0.5. Table 2. 5 lists the selected indicators and the corresponding classification.

Table 2. 5 - Sustainability indicator values

		CGA	CGB	CGT	GLY	Conventional polyol
Environmental indicators						
	Feedstock renewability	1.0	1.0	1.0	0.0	0.0
	Energy intensity	1.0	1.0	0.5	0.0	0.0
	CO_2 balance	1.0	1.0	0.5	0.0	0.0
	Wastes	1.0	1.0	0.5	0.0	0.0
Economic indicators						
	Yield	1.0	1.0	1.0	1.0	1.0
	Feedstock prices	1.0	1.0	1.0	0.0	0.0
	Process costs	1.0	1.0	0.5	0.0	0.0
Social indicators						
	Process conditions	1.0	1.0	0.5	0.0	0.0
	Chemical safety	1.0	1.0	0.5	0.0	0.0
	Innovation potential	1.0	1.0	1.0	0.0	0.0
	TOTAL	10.0	10.0	7.0	1.0	1.0

As regards environmental indicators, both unrefined CG samples were classified with 1.0 as CG is a renewable feedstock and a byproduct of the biodiesel industry hence, no energy, CO_2 nor wastes are involved in their production. Yet, CGT resulting from the pretreatment of CG which involves energy, CO_2 emissions and the production of waste (water and salts), was classified in all environmental indicators with 0.5 except for that related with the feedstock renewability. In turn, GLY and the conventional polyol being petroleum based, their production requires the consumption of energy, subsequent CO_2 emissions and yield wastes thus, were classified with 0.0 in all criteria.

In what concerns economic indicators, as the polyols present a yield of 100% they were classified with 1.0. For feedstocks price, both unrefined and pretreated CG were classified with 1.0, whilst GLY and the conventional polyol were classified with 0.0. Production costs however are only classified with 1.0 in the case of unrefined CG, whilst for CGT the classification was 0.5 due to the cost involved in the purification of the raw material, and finally for GLY and the conventional polyol the classification was 0.0 as their production is more complex and expensive.

As for the social indicators, both CGA and CGB were classified with 1 due to the fact that they do not require any processing and don't raise any safety risk and have a significant innovation potential. In turn, for CGT though the innovation potential is ranked with 1.0, the process conditions and safety risks involved with the use of relatively small amounts of sodium hydroxide and sulfuric acid were classified with 0.5. Finally, GLY and the conventional polyol were classified with 0.0 for all social indicators as their production does not involve any innovation potential, the processes are more complex, expensive and hazardous.

Considering the classification attributed to the various indicators listed in Table 2. 5, it can be concluded that the use of unrefined CG samples have the best potential toward sustainability whilst CGT has many positive attributes yet some limitations have to be considered. Conversely, GLY and the conventional polyol have no potential sustainability.

2.5. Conclusions

Ecofriendly PUFs have been produced from different samples of CG to assess the need of additional purification steps. From the results obtained it was concluded that the impurities present in unrefined CG seem to affect the foaming process, the crosslinking density and can have some plasticizing effect. As a result, the mechanical properties of the ensuing foams and the Young's modulus, toughness and compressive stress are lower than those obtained for PUFs derived from pretreated CG. However, a judicious control of the percentage of this type of impurities, reaction parameters and even inorganic fillers can be explored to tune these properties. Moreover, the thermal stability and thermal conductivity are not significantly affected by the presence of fatty acids and esters. Indeed, all CG derived PUFs were thermally stable up to 180 ºC and exhibited low densities and low thermal conductivities hence CG, without any purification step or pre-treatment is a suitable material for the production of PUFs. Additionally the evaluation of the impact of the use of these ecofriendly polyols towards sustainability of foam production yielded promising results. Therefore, these ecofriendly and cheap materials can be of interest for thermal insulation applications especially if some reinforcement fillers are added to improve their mechanical performance.

3. Optimization of the PUFs formulation

This chapter was presented as poster communication (N. V. Gama, C. S. R. Freire, R. Silva, A. Barros-Timmons, C. P. Neto, A. Ferreira, "Rigid polyurethane foams from crude glycerol"), at the 5th Euchems conference, in Instabul, in 2014. Also was published in the journal of Polymer Testing (Nuno V. Gama, Rui Silva, Marco Costa, A. Barros-Timmons, A. Ferreira, Statistical evaluation of the effect of formulation on the properties of crude glycerol polyurethane foams, Polymer Testing, 56, 200-206, (2016)) doi.org/10.1016/j.polymertesting.2016.10.006.

3.1. Abstract

In our pursuit to develop ecofriendly materials, the effect of the main components of the formulation used for the preparation of PUFs derived from unrefined CG has been systematically studied. A series of PUFs has been prepared using formulations with judicious variations of the percentage of each component. The physical properties of the resulting PUFs were measured and the data collected were statically treated using a four-way functional ANOVA method. From the ANOVA results, the paramount importance that the blowing agent and the surfactant have on the regulation of density and thermal conductivity of PUFs was recognized. Regarding the mechanical properties, the isocyanate content presented a dominant influence on the increase of Young modulus, toughness and compressive stress of PUFs.

Keyword: Polyurethane foams; Polyurethane formulation; Crude glycerol, Statistical analysis; ANOVA, Physical properties

3.2. Introduction

PUs are versatile engineering materials which find a wide range of applications because their properties can be readily tailored by the type and composition of their components.[57] PU is the general name for a polymer having urethane linkages in their chain structure resulting from the reaction between NCO groups of an isocyanate and the OH groups of a polyol.[4] The foaming reaction where water is frequently used as blowing agent occurs in parallel to the polymer reaction. The foaming results from its reaction with isocyanate groups, which spontaneously releases carbon dioxide, thus generating bubbles.[11] In that sense, the isocyanate and polyol, as well as catalysts, surfactants and blowing agents are used to regulate the morphology of the cell structures and the mechanical properties of the foams.

Rigid PUFs have been widely used as thermal insulation materials, because the air trapped within the cellular structure develops passive heat absorption capacity. The low thermal conductivity, high mechanical and chemical stability at high and low temperatures are some of their advantages.[3] In turn, it is well established that the mechanical response and thermal properties of these materials depend on their architecture, the cell wall thickness, the size distribution and the shape of the cells, among others.[3,43] Nevertheless, whatever their application, optimization of their formulation is needed, as well as the understanding of the relationship between the microstructure and the mechanical and thermal properties.

Like other polymers, PUs rely on petroleum feedstocks, and the increasing concern over environmental issues as well as the supply of petroleum have motivated the development of PUs from renewable raw materials.[57,132,231,232] Liquefied lignin,[217] cork,[50,220] coffee grounds,[51,97] starch,[218] soybean straw,[219] sugar beet pulp[63] or date seeds[72] have been used as substituents or at least partial substituents of petroleum feedstocks in the synthesis of PUFs, and the results obtained demonstrated that the ensuing foams had comparable foaming kinetics, density, cellular morphology, and thermal conductivity, to those obtained using petroleum derived polyols. Another potential renewable resource that can be used as polyol is CG, which is a byproduct of biodiesel production.[52] The successful replacement of petrochemicals polyols by CG in PUF production has the potential to reduce their cost and environmental impact. The production of PUFs from CG might also contribute to alleviating the current CG glut and contribute to the sustainability of the PUFs industry.

Although the variability of the composition of such raw material could be a constraint, we have recently demonstrated that it is not the case.[52] In fact, adjustments in formulations of PUFs can modulate the properties of the resulting materials.

In the present work, CG was directly used without any pretreatment or purification step as the polyol component in the production of PUFs and different formulations were used to statistically evaluate the influence of the different relative percentages of the components on the properties of the ensuing foams. To the best our knowledge this is the first report on the optimization of the PUFs formulation derived from CG whose effect on the properties of the resulting PUFs was statistically evaluated. The statistical method used was performed by a four-way functional ANOVA, which allows testing the different foam properties according to the quantity of reactants used. The quantity of each reactant are the factors, the properties of the ensuing foams are the dependent variables and the statistical significance level of the model (p-value) used was 0.050.

3.3. Experimental

3.3.1. Materials

The foams studied were produced by reaction of CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. The CG sample was kindly supplied by Bioportdiesel and is composed by 84% of glycerol and 16% of fatty acids and methyl esters with a water content of 1.6 ± 0.01, AV of 23.1 ± 0.2 mg_{KOH}/g and OH_{number} of 399.0 ± 4.7 mg_{KOH}/g. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% (weight percent free isocyanate content), functionality of 2.7, viscosity of 190 mPa.s (at 25 ºC) and an isocyanate equivalent of 135 was kindly supplied by Dow Chemicals. Tegostab B8404, a polyether-modified polysiloxane with a density of 1.045-1.065 g/cm^3 (at 25ºC) was used as silicone surfactant and was supplied by Evonik. Polycat 34, a tertiary amine with a density of 0.84 g/cm^3 (at 25ºC), was used as catalyst and supplied by Air Products. Distilled water was used as blowing agent.

3.3.2. Characterization of crude glycerol

The determination of water content, acid value (AV) and hydroxyl number (OH_{number}) of the polyols samples has been described in Chapter 1.

3.3.3. Production of PUFs

Different amounts of surfactant, catalyst and blowing agent were added to CG and placed in a polypropylene cup. The mixture was homogenized using an IKA Ost Basic mixer with rotating blades for *ca*. 10 seconds at 700 rpm. Different amounts of isocyanate were added to these mixtures and mixing continued. The foams were obtained by free expansion in the cup mold at room temperature. Table 3. 1 lists the amount of each reactant based on 100 parts by mass of CG.

Table 3. 1 - Foam formulations

Sample code [a]	Polyol	Isocyanate (PHP)	Catalyst (PHP)	Surfactant (PHP)	Blowing Agent (PHP)
PUF-130-6-6-5	100	130	6	6	5
PUF-160-6-6-5	100	160	6	6	5
PUF-130-8-6-5	100	130	8	6	5
PUF-160-8-6-5	100	160	8	6	5
PUF-130-6-9-5	100	130	6	9	5
PUF-160-6-9-5	100	160	6	9	5
PUF-130-8-9-5	100	130	8	9	5
PUF-160-8-9-5	100	160	8	9	5
PUF-130-6-6-7	100	130	6	6	7
PUF-160-6-6-7	100	160	6	6	7
PUF-130-8-6-7	100	130	8	6	7
PUF-160-8-6-7	100	160	8	6	7
PUF-130-6-9-7	100	130	6	9	7
PUF-160-6-9-7	100	160	6	9	7
PUF-130-8-9-7	100	130	8	9	7
PUF-160-8-9-7	100	160	8	9	7

[a] *Sample Code (PUF-A-B-C-D): A - wt% of isocyanate; B – wt% of catalyst; C – wt% of surfactant; D – wt% of blowing agent*

3.3.4. Characterization of PUFs

Each foam was characterized by Scanning Electron Microscopy (SEM), density, thermal conductivity measurements and compressive tests according to procedures and conditions described in Chapter 1

3.4. Results and discussion

In order to get a better understanding of the influence of the different components and respective relative percentages on the properties of PUFs, different formulations were used, and the resulting PUFs were characterized by density, thermal conductivity and mechanical tests. Their properties are listed in Table 3. 2.

Table 3. 2 - Effect of each reagent on PUFs properties (mean and standard deviation)

Sample code	Density (kg/m^3) Accuracy ± 0.1 mg	Thermal conductivity (W/mK) Accuracy ± 10%	Young Modulus (kPa) Accuracy ± 0.5%	Toughness (J/m^3) Accuracy ± 0.5%	Compressive stress σ10% (kPa) Accuracy ± 0.5%
PUF-130-6-6-5	51.9	0.049	309	4857	17.8
PUF-160-6-6-5	50.7	0.045	344	5235	19.6
PUF-130-8-6-5	45.5	0.051	331	4683	18.6
PUF-160-8-6-5	42.0	0.051	457	6035	19.9
PUF-130-6-9-5	51.5	0.040	338	4957	18.4
PUF-160-6-9-5	34.8	0.038	382	5207	19.5
PUF-130-8-9-5	36.7	0.043	367	5769	19.6
PUF-160-8-9-5	33.0	0.041	439	7050	21.7
PUF-130-6-6-7	38.0	0.042	311	5127	18.9
PUF-160-6-6-7	35.6	0.039	363	5463	19.9
PUF-130-8-6-7	41.8	0.043	323	5248	18.3
PUF-160-8-6-7	31.7	0.039	446	6738	20.2
PUF-130-6-9-7	33.2	0.040	349	5535	18.8
PUF-160-6-9-7	36.5	0.037	471	6483	20.2
PUF-130-8-9-7	35.4	0.037	350	5968	20.8
PUF-160-8-9-7	31.7	0.036	508	6537	21.8

As it can be seen from Table 3. 2, the use of different formulations results in foams with different properties, which will be discussed further. To obtain a clearer understanding of the influence of each reactant on the properties of the ensuing foams, statistical analysis was carried out using a 4-way ANOVA, using the IBM SPSS version 22. The density, thermal conductivity, Young modulus, toughness and compressive stress were used as dependent variables, while the isocyanate (*Iso*), catalyst (*Cat*), surfactant (*Surf*) and blowing agent (*BA*) were used as independent variables. p-values less than 0.05 were considered statistically significant and the results obtained are presented in Table 3. 3 and Figure 3. 1.

Table 3. 3 - 4-way ANOVA results

Independent variables	**Dependent variables**														
	Density			Thermal conductivity			Young modulus			Toughness			Compressive stress		
	SS	df	p-value	SS	df	p-value	SS	df	p-value	SS	df	p-value	SS	df	p-value
Corrected model	524.8	4	0.057	0.00E+00	4	0.059	4.92E+04	4	0.000	6.14E+06	4	0.001	16.7	4	0.000
Iso	89.3	1		2.26E-05	1		3.34E+04	1		2.73E+06	1		8.4	1	
Cat	73.1	1	0.081	7.56E-06	1	0.249	7.92E+03	1	0.013	1.67E+06	1	0.006	3.8	1	0.005
Surf	122.1	1	0.030	1.38E-04	1	0.000	6.43E+03	1	0.022	1.06E+06	1	0.022	3.6	1	0.006
BA	240.2	1	0.005	1.27E-04	1	0.000	1.49E+03	1	0.227	6.83E+05	1	0.055	0.9	1	0.114
Interactions	217.6	11		5.62E-05	11		1.00E+04	11		1.63E+06	11		3.4	11	
Total	25532.8	16		2.85E-02	16		2.38E+06	16		5.24E+08	16		6182.3	16	
Total corrected	742.3	15		3.51E-04	15		5.93E+04	15		7.77E+06	15		20.1	15	
R	0.707			0.804			0.831			0.790			0.833		

SS: sum of squares; df: degree of freedom; p-value: indicates insignificant value at 95% confidence level.

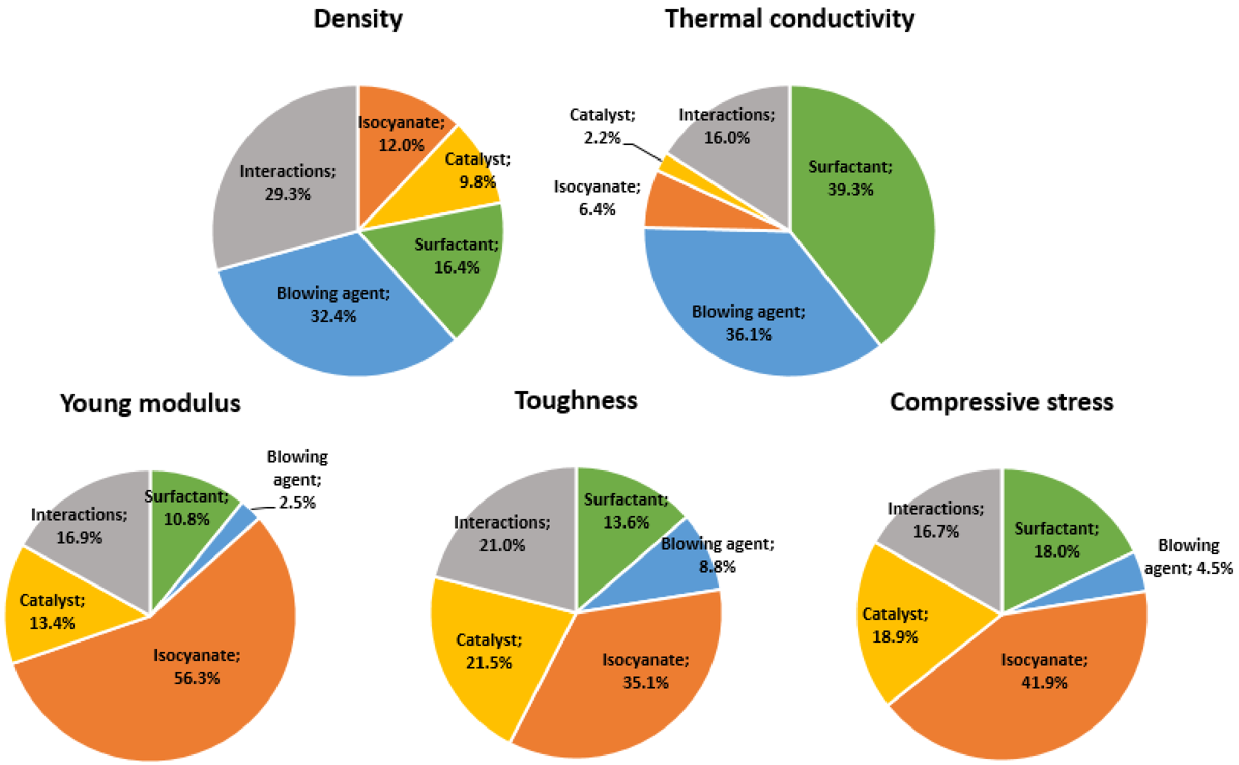
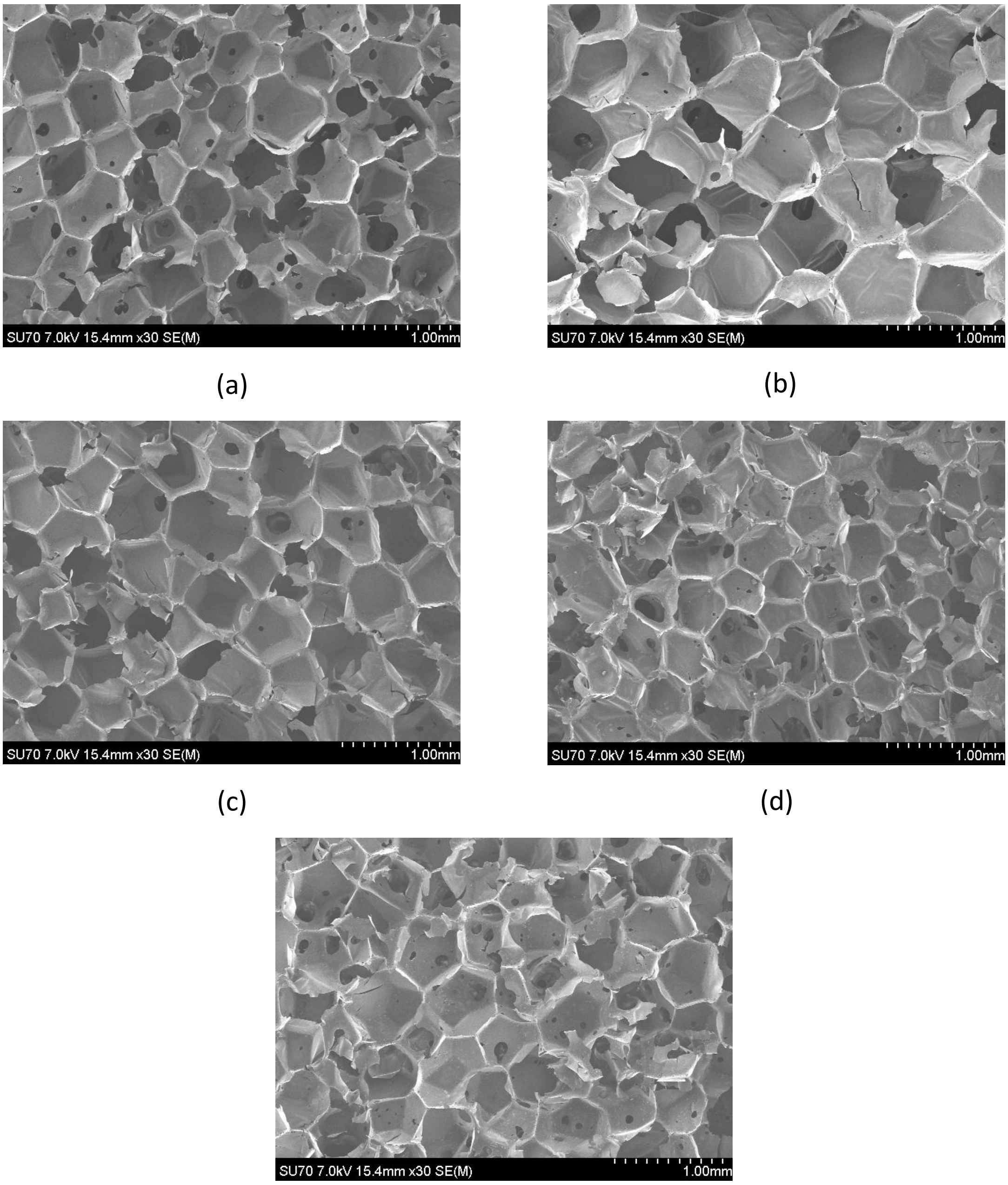


Figure 3. 1 - Relative effect sizes (Eta squared) of the formulation components on the properties of the foams

3.4.1. Density

The density of foams is primarily dependent on the quantity of gas released during the reaction. This property of foams is particularly important because it affects their thermal conductivity and mechanical properties. Since water was used as a blowing agent to produce CO_2 from the reaction with the isocyanate [233], both blowing agent and isocyanate content play an important role in the expansion of the foams and, therefore, in their density. From SEM images, the typical cellular structure obtained during foam formation is clearly observed in all foams and it is also noticeable that the foam cells are mainly closed. However, some differences can be noticed.

From Table 3. 2, it can be seen that the density of PUFs decreased with the increase of the amount of blowing agent. The same observations have been reported by H. C. Jung *et* *al.*[234] This can also be observed from SEM images presented in Figure 3. 2, since the increase of the blowing agent increased the average diameter of the cells (see Figure 3. 2 (a) and (b)).



(a) (b) (c) (d) (e)

Figure 3. 2 - SEM micrograph of PUF-130-6-6-5 (a), PUF-130-6-6-7 (b), PUF-160-6-6-5 (c), PUF- PUF-130-6-9-5 (d) and PUF-130-8-6-5 (e)

From these images it is proved that the use of higher amounts of blowing agent leads to the formation of bigger bubbles.[235] The cell diameter increased from 4.9 ± 0.6 µm (PUF-130-6-6-5) up to 6.6 ± 0.8 µm (PUF-130-6-6-7) with the increase of the blowing agent. The influence of the blowing agent on the density of the foams is also highlighted in Figure 3. 1, since the blowing agent has the most relevant effect on the density of PUFs (32.4% of influence). Furthermore, the p-value associated with this result, 0.005, demonstrates its high statistical significance (see Table 3. 3).

Sung Hee Kim *et al.* reported that foam density decreased as the isocyanate content increased, due to the additional CO_2 produced.[236] This relationship is in agreement with the results presented in Table 3. 2. Indeed, from Figure 3. 1, the influence (12.0%) that the isocyanate content has on the density of the foams can be observed and the p-value associated with this parameter is close to the statistical significance (p-value = 0.057). From Figure 3. 2, it can be also be seen that the increase of the isocyanate content increased the diameter of the pores. Comparing Figure 3. 2 (a) and (c), which were produced using different isocyanate contents, no major differences on the structure homogeneity can be observed. However, PUF-130-6-6-5 presents an average cell diameter of 4.9 ± 0.6 µm, while PUF-160-6-6-5 presents an average diameter of 5.6 ± 0.7 µm, but the difference in density between these two samples may be more associated with the ratio between open/closed cells.

A similar trend was observed for the surfactant content, considering that the density of PUFs decreased with the increase of surfactant content (see Table 3. 2). Indeed, the role of the surfactant is to control the process of foaming, producing more cells with smaller size as well as regulating the ratio of open/close cells.[51] Figure 3. 2 (a) and (d), corresponding to foams prepared using different surfactant content, confirm that the cellular structure of PUF-130-6-9-5 is more regular, with more cells with smaller diameters. However, the ratio between closed and open cells may have a significant role too. [235] This implies that the foaming process efficiency is improved by the addition of surfactant due to its ability to create nuclei and to augment the stability of the foams. Indeed, in Figure 3. 1, it is shown that the influence of the surfactant on the density is relevant (16.4%) and actually has statistical significant (p-value = 0.030). A similar observation was obtained by B. K. Kim *et al.* who reported that the density decreases rapidly due to the efficiency of the surfactant.[237]

Finally, it was also observed that the increase of the catalyst amount, decreased the density of the resulting foams (see Table 3. 2). The catalyst promotes, not only the reaction between the isocyanate with polyol, but also the reaction of the isocyanate with water. Moreover, an increase of catalyst content can result in an incresase of reaction kinetic, which can promote the microphase separation affecting the foam morphology and consequently the mechanical properties of the PUF. However, from the results obtained, it was observed that the catalyst plays a secondary role in the foam expansion, confirmed by its low influence (9.8%) which actually does not have any statistical significance (p-value = 0.081). Comparing Figure 3. 2 (a) and (e), which correspond to foams prepared with different percentage of catalyst, it can be observed that in the latter presents poor cellular homogeneity. This can be attributed to the fact that the use of more catalyst increased the kinetic of the polymer reaction, whilst the foaming process was not fast enough for the cells to grow properly. For this reason, small differences in diameter and ratio between open/closed cells can cause some differences in density.

3.4.2. Thermal conductivity

For insulation applications, the thermal conductivity (*k*) of PUFs is a property of paramount importance and it is related to the foam density, the ratio of open/closed cells and the thermal conductivity of the gas used as blowing agent, among others. Whilst the whole foam only contains a small fraction of PU and its *k* value is much higher than that of the blowing gas, higher density foams have higher thermal conductivity.[238] In turn, if more blowing gas is trapped within the foam pores, there is less thermal conductive material, as claimed by Kun Hyung Choe *et al.*[239] The results obtained for the PUFs prepared using different formulations presented in Table 3. 2 confirm that an increase of blowing agent content decreased the thermal conductivity of PUFs. The influence of 36.1% and its statistically significance (p-value = 0.000), proves the importance of the blowing agent on the thermal conductivity of the foams.

As regards the isocyanate, it is known that it plays a relevant role on the density of the foams, so it was expected that it also has some influence on thermal conductivity. In fact, as in the case of density, Sung Hee Kim *et al.* reported a thermal conductivity decrease with increase of isocyanate index,[236] and this is in agreement with the results presented in Table 3. 2. However, from Figure 3. 1, it can be seen that its influence only represents 6.4% and, from Table 3. 3, it can be seen that this parameter is not statistically significant (p-value = 0.059). This is due to the fact that the whole foam only contains a small fraction of PU.

Conversely, the percentage of the surfactant has a marked influence on the thermal conductivity of the foams, due to the role that the surfactant plays in the foaming process and its impact on the cells structure, cell walls thickness and open/close cell ratio.[240] From Table 3. 2, it can be observed that the increase of the surfactant content lowers the thermal conductivity. The same conclusion can be found in literature.[237] Undoubtedly, the influence of surfactant on the thermal conductivity of the foams is highlighted in Figure 3. 1, representing 39.3% of influence. Also, Table 3. 3 demonstrate its high statistically significance (p-value = 0.000).

Finally, the percentage of catalyst has little influence on the thermal conductivity of the foams nor statistical significance.

3.4.3. Mechanical properties

A combination of low density, low thermal conductivity and good mechanical properties is required for PUFs to be used for thermal insulation applications [225] but, whatever their use, optimization of their mechanical properties requires good understanding of the effect of the different components of formulation. In fact, the mechanical response of this type of material is very complex, since it depends on their architecture, the intrinsic properties of the polymer, the cell wall thickness, the size distribution and the shape of the cells, among others.

The relationship between the mechanical response of PUFs and the intrinsic properties of the polymer, is associated with the molecular composition of PU, which consists of soft and hard segments. The urethane and urea groups form the hard-segment, while the soft segments consist of aliphatic polyol chains.[159] Therefore, higher isocyanate amounts yield more urethane groups, making the PUFs more rigid.[218] Similarly, higher contents of blowing agent (water) leads to an increase of urea linkages in the final polymer [234] making the polymer stiffer. Figure 3. 3 shows the most representative compressive stress-strain curves obtained for foams prepared using varying the amounts of isocyanate, catalyst, surfactant and blowing agent. The values obtained for Young's modulus, compressive stress and toughness for all PUFs are summarized in Table 3. 3.

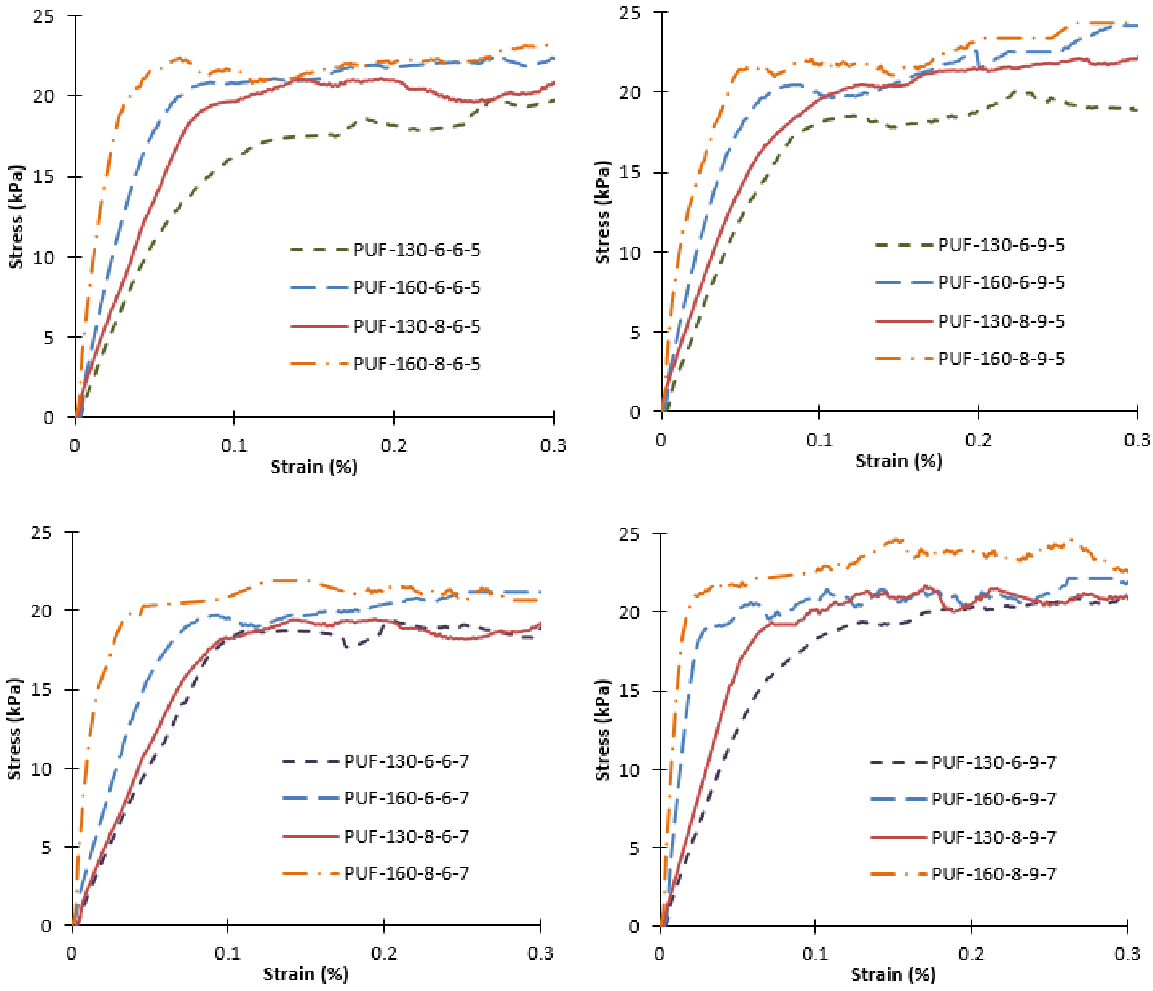


Figure 3. 3 - Compressive stress-strain curves of PUFs

As can be observed, the increase of isocyanate content lead to increase of the Young's modulus, toughness and compressive stress, which is in agreement with the results reported by Park *et al.* [241] regarding an increase in compressive strength of PUFs when the isocyanate content was increased within the same range used in this study. This is also verified by the statistical analysis which show that the isocyanate content has an influence of 56.3% on the Young's modulus, 35.1% on the toughness and 41.9% on the compressive stress (see Figure 3. 1). Additionally, all these results have high statistical significance (p-value of Young's modulus = 0.000, p-value of toughness = 0.001 and p-value of compressive stress = 0.000).

As regards the effect of the blowing agent, Figure 3. 3 and, more importantly, the ANOVA results show that it only has a marginal effect on the Young's modulus (2.5%) and compressive stress (4.5%), with a slightly effect on the toughness (8.8%). However, the results have not statistically significant as the corresponding p-values are higher than 0.050. These results are particularly interesting as it is normally assumed that, when water is used, the formation of urea groups may be associated with an increase in stiffness, as reported for example by H. C. Jung *et al.* [234]

In the literature, it is reported that an increase of surfactant content causes a remarkable increment of the force required for 10 % deformation.[237] The increase of stiffness with the increase surfactant content can be associated to the quantity of retained gases. From the results presented in Table 3. 2 and Figure 3. 3, this increment of the stiffness of the foams can also be observed with the increase of the surfactant amount. Also from Figure 3. 1, it can be observed that the surfactant has an effect of 10.8% on the Young's modulus, 13.6% on the toughness and 18.0% on the compressive stress. All these results presented p-value lower than 0.050, indicating their statistical significance.

Finally, with respect to the catalyst influence, the results obtained show that it has a relevant influence on the Young's modulus, toughness and compressive stress (13.4%, 21.5% and 18.9%, respectively) and all these results are statistically significant (p-value of 0.013, 0.006 and 0.005, respectively), as illustrated by Figure 3. 1 and Table 3. 3. Kun Hyung Choe *et al.* have also reported that the compressive strength of PUFs increases with the catalyst content and have attributed that increase to the fact that the catalyst promotes the production of urethane groups (by the reaction between the isocyanate with the polyol) and urea groups (by the reaction between the isocyanate with water) which belong~~s~~ to the hard segments. [239] As mentioned before, the mechanical properties of the foams are intrinsically dependent on density, hence, to exclude the effect of density variations, normalized values of the Young's modulus (specific Young's modulus), toughness (specific toughness) and compressive stress (specific compressive stress) and have been determined and the results are presented in the Table 3. 4.

Table 3. 4 - Young's modulus, compressive stress (σ10%) and toughness normalized for density

Sample code	Specific Young modulus (m^2/s^2)	Specific toughness (m^2/s^2)	Specific compressive stress (m^2/s^2)
PUF-130-6-6-5	6.0	93.6	0.343
PUF-160-6-6-5	6.8	103.3	0.387
PUF-130-8-6-5	7.3	102.9	0.409
PUF-160-8-6-5	10.9	143.7	0.474
PUF-130-6-9-5	6.6	96.3	0.357
PUF-160-6-9-5	11.0	149.6	0.560
PUF-130-8-9-5	10.0	157.2	0.534
PUF-160-8-9-5	13.3	213.6	0.658
PUF-130-6-6-7	8.2	134.9	0.524
PUF-160-6-6-7	10.2	153.5	0.531
PUF-130-8-6-7	7.7	125.6	0.438
PUF-160-8-6-7	14.1	212.6	0.637
PUF-130-6-9-7	10.5	166.7	0.566
PUF-160-6-9-7	12.9	177.6	0.553
PUF-130-8-9-7	9.9	168.6	0.588
PUF-160-8-9-7	16.0	206.2	0.688

From the results listed in Table 3. 4, it is clear that, despite of the density effects, the variation of the reactants amounts studied have a direct effect on the mechanical properties of the foams, increasing the Young's modulus, toughness and compressive stress.

3.5. Conclusions

The rationale to fine tune formulations of PUFs derived from unrefined CG in order to modulate their physical properties has been established using statistical analysis. The results obtained proved that both density and thermal conductivity are governed by the blowing agent and surfactant contents. In turn, the mechanical properties are essentially determined by the content of isocyanate and catalyst. Therefore, the implementation of such a systematic approach will contribute to the sustainability of the PUF industry.

4. Development of CG derived composite foams for enhanced energy efficiency

This chapter was presented as oral communication (N. V. Gama, A. Barros-Timmons, J. A. P. Coutinho, C. Amaral, T. Silva, R. Vicente, A. Ferreira, "Enhancement of thermal properties of crude glycerol polyurethane foams"), at the AAMC conference, in Miami in 2016.

4.1. Abstract

The aim of this study was to enhance the thermal properties of CG derived PUFs using PCMs. The main challenge of filling PUFs with PCM is to combine the low conductivity of PUFs and simultaneously take advantage of the heat released/absorbed by PCMs. The solution considered was to add expanded graphite (EG) to the composite to promote thermal conductivity in order to take advantage of PCMs ability to store/release heat. However filling the PUFs with PCM and/or EG increased severely both thermal conductivity and density of the materials which did not improve their thermal energy storage.

Keyword*:* Polyurethane foams; Crude glycerol, PCMs, Expanded graphite, Numerical simulation

4.2. Introduction

The primary role of buildings is to protect the mankind from the climates changes by keeping the inside of buildings cool in the summer and warm in the winter. Thermal energy storage is essential for these two solutions.[186,242–244] PUs are versatile engineering materials which find a wide range of applications and are very commonly found in our everyday life due to their applications namely as thermal insulating material. Within this spectrum, rigid PU foams (PUFs) are an important class of materials due to their outstanding thermal insulation properties.[171] Compared with other insulation materials, PUFs are highly competitive and if heat storage materials are additionally incorporated into PUFs, the heat loss to as well as gain from surrounding will be reduced and the energy saving will be much more efficient.[170–173]

In the last years, this concept has found growing interest as a result of the rise of a new class of materials. They are so-called PCMs. PCMs, which are also called latent heat-storage materials, have high capability to store and release large heat energy within a slight or no temperature changes. According to their phase change states, they fall into three groups: solid–solid PCMs, solid–liquid PCMs and liquid–gas PCMs. In solid–liquid PCMs, the energy is absorbed by the breakdown of the bonding responsible for the solid structure. A large amount of heat is absorbed during the phase change with no increase of temperature. When the materials cool down, the latent heat will be released to the surroundings and the PCMs returns to its solid state.[171,177,179,181–183]

The low thermal conductivity of PCMs requires the use of large and expensive heat transfer surfaces, which is considered its major drawback.[188] Hence, in order to enhance the action of PCMs, the thermal conductivity of PUFs must be increased and one option to achieve this is filling the polymer with conductive agents. Thermal conductive carbon based materials such as expanded graphite (EG) present several advantages over the usual metal fillers due to lower costs, corrosion resistance, less material requirement for percolation, and ease of processing.[189] In that sense, the addition of EG allows to increase thermal conductivity and subsquential enhancing the action of PCMs, whilst improving their flame retardant and mechanical properties.

The use of PCMs has been widely studied,[188] but due to their price it not viable to fill PUFs with PCMs in large scale. Therefore, numerical simulation must be developed to optimize composites formulations and thickness of the active layer towards the best environmental contribution.[245]

The use of PUF filled with PCM and EG to enhance the thermal efficiency of building, per se, consists in a contribution to sustainability, especially if the raw material for the production of PUFs are from renewable resources. Indeed, polyols derived from acid liquefied or oxypropylated biomass have been used to replacing petroleum based polyols in the synthesis of PUFs.[47,50,51,56,57,97,220,246] More recently, CG has been used for the production of PUFs.[52,54,157] The successful replacement of petrochemicals by CG in the PUFs production has the potential to reduce it costs and environmental impact.

In the present work we study the enhancement of thermal properties of CG derived PUFs. The main challenge of filling PUFs with PCM is to combine the low conductivity of PUFs and simultaneously take advantage of the heat released/absorbed by PCMs. The solution was achieved by adding EG to the composite to promote thermal conductivity in order to take advantage of PCMs. The resulting foams were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), density, thermal conductivity, compressive strength, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Also a numerical simulation was developed to study the effect of the composite on the thermal insulation material and to optimize the thickness of the active layer towards the best environmental contribution.

4.3. Experimental

4.3.1. Materials

The foams studied were produced from the reaction between CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. CG sample was kindly supplied by Bioportdiesel and present a water content of 1.6 ± 0.01, an *AV* of 23.1 ± 0.2 $mg_{KOH}.g^{-1}$ and an OH_{number} of 399.0 ± 4.7 $mg_{KOH}.g^{-1}$. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% (weight percent free isocyanate content), with a functionality of 2.7, a viscosity of 190 mPa.s (at 25 ºC) and an isocyanate equivalent of 135 was kindly supplied by Dow Chemicals. Tegostab B8404, a polyether-modified polysiloxane with a density of 1.045-1.065 $g.cm^{-3}$ (at 25ºC) was used as silicone surfactant and was supplied by Evonik. Polycat 34, a tertiary amine with a density of 0.84 $g.cm^{-3}$ (at 25ºC), was used as catalyst and supplied by Air Products. As blowing agent, distilled water was used. A micro encapsulated parafine wax (Micronal DS 5008 X) with a density of 250–350 kg/m^3 and a melting point of 26.2 ºC was supplied by BASF and used as PCM. EG (EG GHL PX 95) with a thermal conductivity of 0.290 mW/mK (at room temperature) and a density of 0.5436 g/cm^3 was supplied by LUH.

4.3.2. Characterization of crude glycerol

The acid value (*AV*), hydroxyl value (*OH number*) and the water content of the polyols were determined according to the procedures described in Chapter 1.

4.3.3. Production of PUFs

In the production of PUF, CG, surfactant, catalyst and blowing agent were placed in a polypropylene cup. The mixture was homogenized using an IKA Ost Basic mixer with rotating blades, for about 10 seconds at 700 rpm. Next the appropriate amount of isocyanate to obtain a $R_{NCO/OH}$=1.10 (ratio between NCO groups of isocyanate and OH groups) was placed in the polypropylene cup and homogenized again. The $R_{NCO/OH}$ used in the PUFs production were determined using Eq. (11).

$$R_{NCO/OH} = (m_{iso} \times \%_{NCO}/M_{NCO})/(m_{polyol} \times (OH_{number} + AV)/M_{KOH} + (m_{H2O} + m_{BA}) \times Eq_{H2O}) \qquad \text{(Eq. 11)}$$

Where $R_{NCO/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH moles of the polyol and water. m_{iso} is the mass (g) of isocyanate, %NCO is the quantity of NCO groups in the isocyanate (31.1%) and M_{NCO} is the molecular weight of NCO group (0.042 g/mmol). m_{polyol} is the mass (g) of each polyol, OH_{number} and *AV* are the hydroxyl number and the acid value of each polyol respectively (mg$_{KOH}$/g). M_{KOH} is the molecular weight of KOH (56.1 mg/mmol). m_{H2O} is the mass of water present in the polyol while m_{BA} is the mass of blowing agent (water) added. Finally, Eq_{H2O} is the equivalent of OH groups present in the water (111 mmol/g).

In the production of PUF filled with EG, EG was dispersed in the appropriated amount of MDI for 30 min using a Sonics Vibra Cell sonicator, while in the production of PUF filled with PCM, the PCMs were added to the polyol component.

PUFs formulations are listed in Table 4. 1.

Table 4. 1 - Foam formulations

Sample [a]	CG	Isocyanate (PHP)	Catalyst (PHP)	Surfactant (PHP)	Blowing Agent (PHP)	EG (wt/wt)	PCM (wt/wt)
PUF	100	209	3	4	4.4	0.0	0.0
PUF-EG0.50	100	209	3	4	4.4	1.4	0.0
PUF-EG0.75	100	209	3	4	4.4	2.0	0.0
PUF-EG1.00	100	209	3	4	4.4	2.7	0.0
PUF-EG1.25	100	209	3	4	4.4	3.4	0.0
PUF-EG1.50	100	209	3	4	4.4	4.1	0.0
PUF-PCM2.5	100	209	3	4	4.4	0.0	6.9
PUF-PCM5.0	100	209	3	4	4.4	0.0	14.2
PUF-PCM7.5	100	209	3	4	4.4	0.0	21.9
PUF-PCM10.0	100	209	3	4	4.4	0.0	29.9
PUF-EG1.00-PCM5.0	100	209	3	4	4.4	2.9	14.3

[a] *Sample Code (PUF-EGX-PCMY): X - wt% of EG; Y – wt% of PCM*

4.3.4. Characterization of PUFs

The thermal conductivity, SEM analysis, FTIR, density, mechanical properties, DMA, TGA and DSC of the foams were determined according to the procedures described in Chapter 1.

4.3.5. Numerical modelling

The PUF panel is located in between the two chambers (warm chamber and cold chamber) at the center of the model. The specimen wall divides the chamber in two parts. The chamber consists of three regions: the cold chamber, the mounting ring and the warm chamber as shown in Figure 4. 1. The chamber walls are composed by three layers: an inner steel sheeting, rockwool insulation and an external zinc sheeting and protection. The thickness of these three layers are 1.5 mm, 10 mm and 1.5 mm respectively. The materials, thickness and thermal properties of the PUF panels and chamber walls are listed in Table 4. 2.

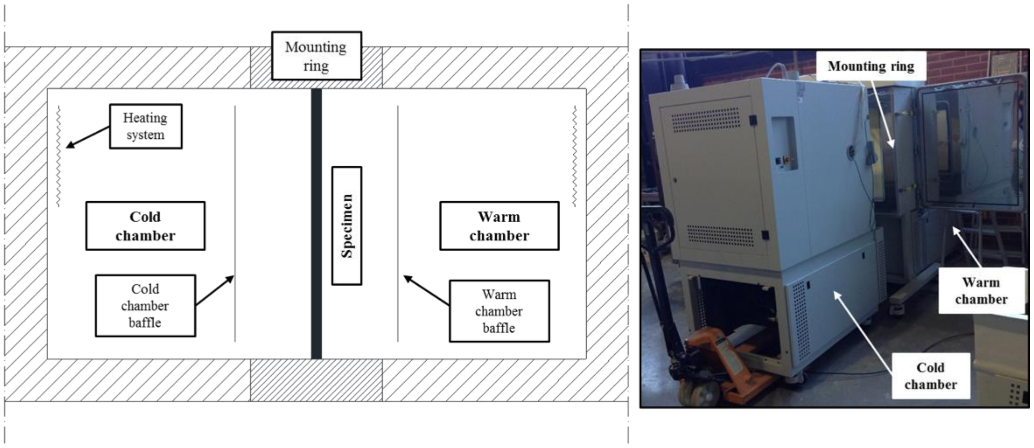


Figure 4. 1 - Scheme of the experimental setup

Table 4. 2 - Thermal properties of the chamber walls and PUF panels

Material	Thickness (mm)	Density (kg/m^3)	Thermal conductivity (W/m.K)	Specific heat (J/kgºC)
Steel	1.5	7900	14.9	477
Rockwool	10	105	0.042	840
Zinc	1.5	7140	116	389
PUF	20	43.8	0.035	833
PUF-PCM5.0	20	91.9	0.037	1620
PUF-EG1.00-PCM5.0	20	115.4	0.044	1666
Interior air	-	7833	54	465

The 2D models were built with the Solidworks software – as plain surfaces – and the modelled file was exported to ANSYS DesignModeler. In order to reduce computational time calculations, the cold chamber was not considered, and the metering conditions were applied on the external face of the PUF panel, as shown in Figure 4. 2. The metering conditions considered on the external face was a temperature profile, T2, presented in Figure 4. 11. The temperatures of the warm chamber were measured, considering three points, according to Figure 4. 3.

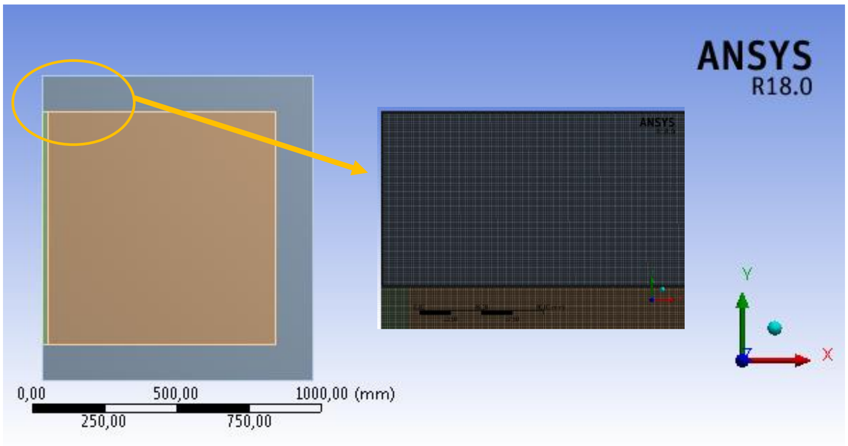


Figure 4. 2 - Numerical model

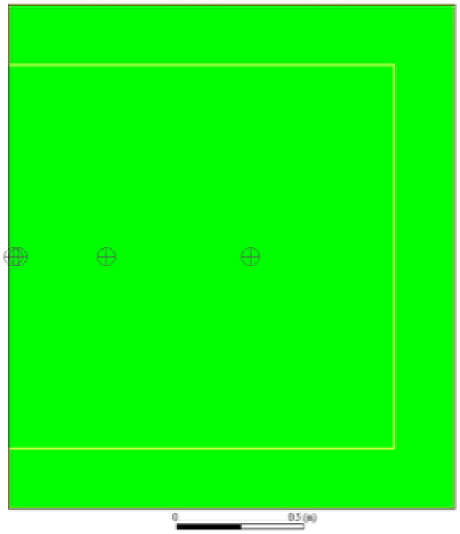


Figure 4. 3 - Measured points positioning in numerical model

4.3.6. Numerical validation with experimental results

To support the validation of the numerical model, an experimental testing was carried out. For the first numerical models was taken into account the follow specifications:

The input of the model is the experimental curve temperature versus time of the metering chamber (warm chamber) and the room temperature variation (around the chambers in laboratory conditions). The former is a trapezoidal temperature wave ranges between 12°C and 52°C; with a period equal to one day cycle with 6 hours steps. A total number of 4 days are considered. The room temperature is around 18°C±2ºC. The input temperature has been taken from the experimental thermocouples placed in the cold chamber and the room temperature from a reference thermocouple in the laboratory.

The final output is the temperature curve in the warm chamber, the average temperature taken from the PT 100 probes positioned 150 mm away from the panel in the warm chamber. The numerical and experimental temperature curves show a good agreement (see Figure 4. 11).

4.3.7. Panel optimization

Once the model validated with experimental data, in order to evaluate the function and performance of the PCMs incorporated into the PUF panel and to analyze their optimum working conditions, a parametric calculation was carried out. The input variable defined was the mass fraction of PCMs (0% and 5%).

4.4. Results and discussion

The aim of this study is to enhance the thermal insulation properties of CG derived PUFs, via the incorporation of PCMs. To overcome the low thermal conductivity of the neat foam and improve the efficiency of PCMs, EG was added to the composites. First, the amount of EG must be optimized by studying its influence on the thermal conductivity of PUFs. In parallel, the effect of PCMs on the morphology, mechanical properties and on the enthalpy of PUF was also assessed. Finally, the selected amounts of EG (1%) and PCM (5%) were used to produce a PUF composite with enhanced thermal properties.

4.4.1. Thermal conductivity

PUFs are essentially used as insulating materials and for insulation applications. In that sense the thermal conductivity (*k*) is a property of paramount importance which in turn is related to the foams density, the ratio of open/closed cells and the thermal conductivity of the gas used as blowing agent. Whilst the whole foam only contains a small fraction of PU, since its *k* value is much higher than that of the blowing agent, higher density foams have higher thermal conductivity. However, EG itself has a high thermal conductivity (0.290 W/mk) so its presence is expected to increase the PUFs thermal conductivity. From Table 4. 3 and Figure 4. 4, it can be seen that the neat foam (PUF) has a thermal conductivity of 0.035 W/mK.

Due to the low thermal conductivity of the foam, higher heat transfer rates are required to the heat reach the PCMs and thereby to fully benefit their action. This objective was accomplish using EG. The thermal conductivity of PUFs filled with EG increased up to 0.042 W/mK at 1% (w/w) of EG. This is increment of thermal conductivity by using EG in agreement with the literature.[247] After that the thermal conductivity reach a plateau. Above this value, a plateau is reached which could be associated with the formation of an EG network and means that the addition of higher %EG is not an advantage. For this reason, 1% (w/w) of EG was chosen to improve the action of PCMs.

On the order hand, from Table 4. 3 it can be seen that the addition of PCMs do not has a significant influence on the thermal conductivity of the ensuing foams, being the slight increase of the thermal conductivity is related to the increase of the density of the foams.

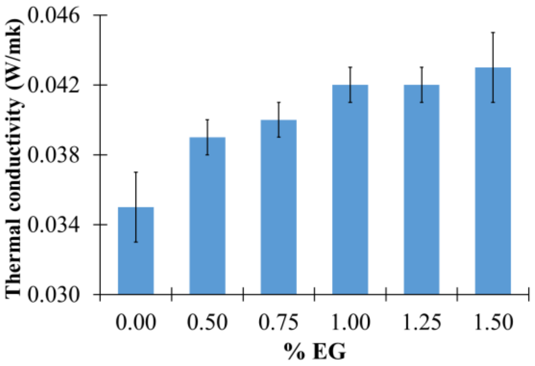
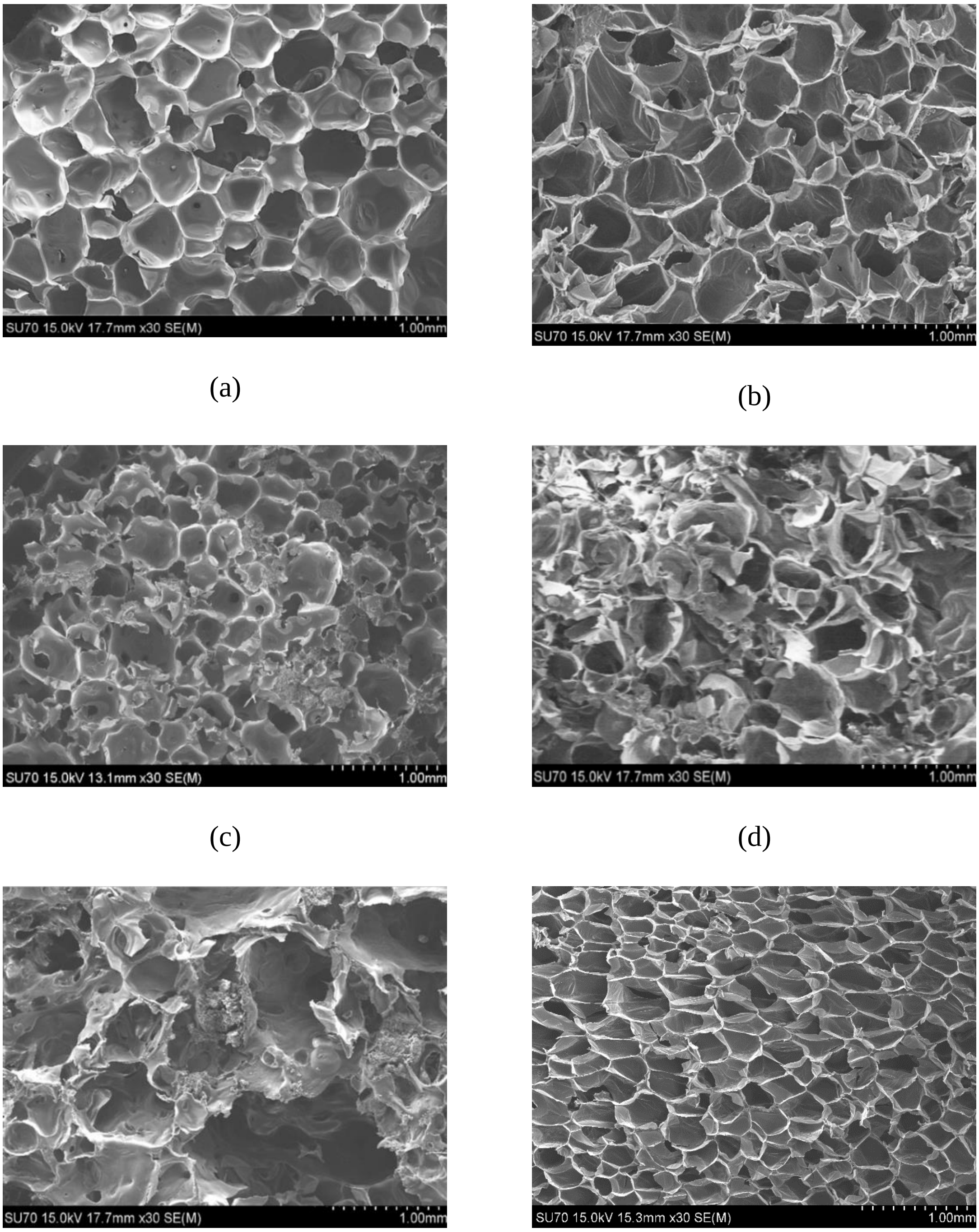


Figure 4. 4 - Thermal conductivity of EG of foams

4.4.2. Morphology

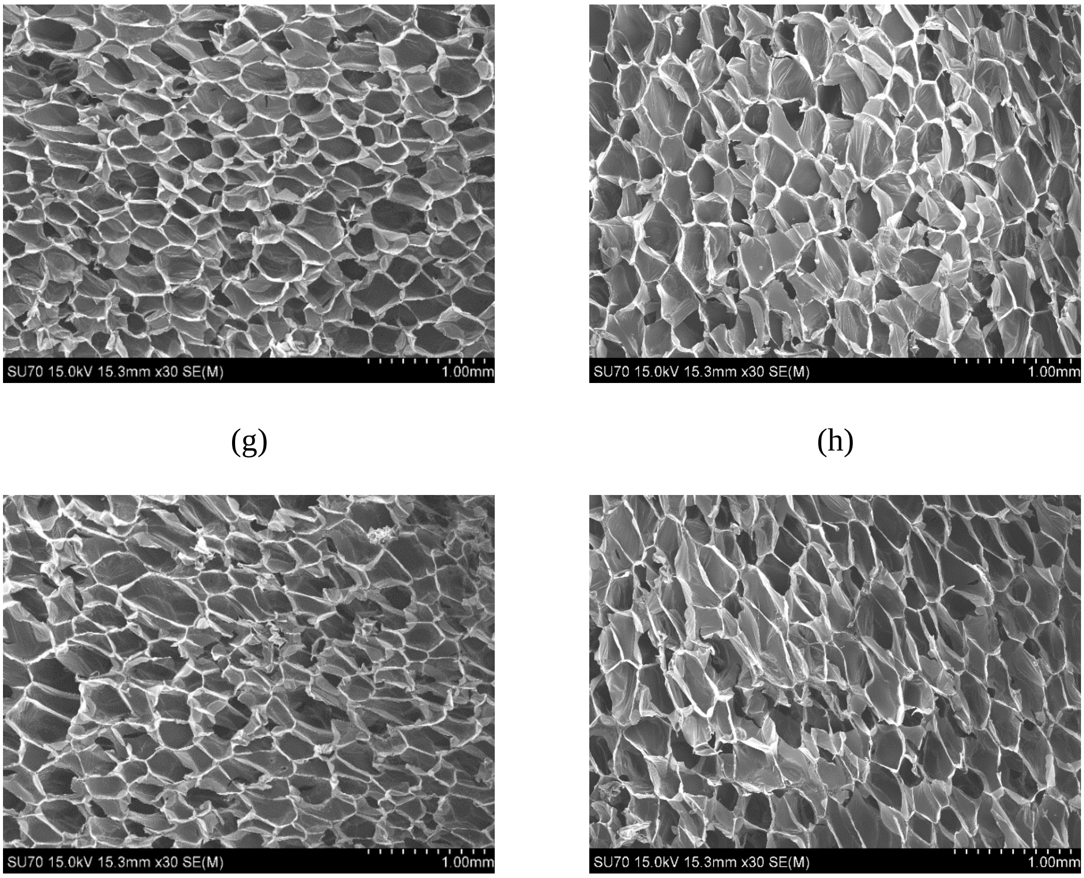
SEM analysis is an important and versatile tool to inspect the foam structure. During mixing, air bubbles are usually introduced in the reaction mixture and act as nucleation sites for the blowing gas generated from the reaction between isocyanate and blowing agent. The bubbles grow resulting in a closely packed network of bubbles responsible for the typical cellular structure of PUFs.[218] The cellular structure of PUF were observed using a scanning electron microscope at a magnification of x30 and is showed in Figure 4. 5.



(a) (b)

(c) (d)

(e) (f)



(g) (h)

(i) (j)

Figure 4. 5 - Micrograph of PUF (a), PUF-PCM2.5 (b), PUF-PCM5.0 (c), PUF-PCM7.5 (d PUF-PCM10.0 (e), PUF-EG0.50 (f), PUF-EG0.75 (g), PUF-EG1.00 (h), PUF-EG1.25 (i) and PUF-EG1.50 (j)

From Figure 4. 5 it is noticeable that the typical cellular structure obtained during foam formation. However, it is clear that the increase of the PCMs content increase their heterogeneity. The irregularity of the cellular structure is related to the fact that the PCMs content can affect the foaming process due to interactions between the polymer matrix and nanoparticles during bubble nucleation and stabilization stages.[248] Similar cases have been reported by others in the literature.[199] Due to their effect on structure of foams, the 5% of PCMs content was selected.

4.4.3. Monitorization of reaction

FTIR analysis was used to monitor the formation of the urethane linkage, as a result of the reaction between the NCO groups of isocyanate and OH groups of CG as well as monitor the extent of this reaction. The FTIR spectra of PUFs were collected on a Perkin Elmer FTIR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. All data were recorded at room temperature, in the range 4000 to 600 cm^{-1} by accumulating 32 scans with a resolution of 4 cm^{-1}. Figure 4. 6 shows the normalized FTIR spectra of PUF, PUF-EG1.00, PUF-PCM5.0 and PUF-EG1.00-PCM5.0.

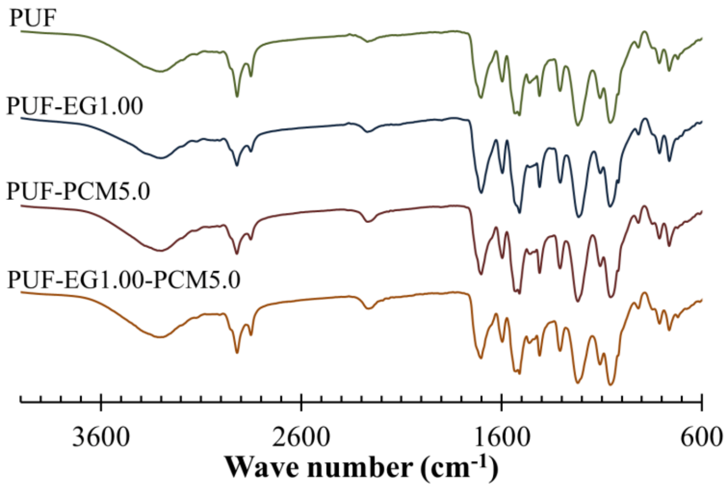


Figure 4. 6 - Normalized FTIR spectra of PUFs

Comparing the normalized FTIR spectra of PUFs it can be seemed that all present a very similar profile, the band in the 3200–3450 cm^{-1} region is attributed to the non-bonded stretching vibrations of O-H groups and symmetric and asymmetric stretching vibrations of the N-H of the urethane and of urea groups (resulting from the reaction between water and some of the isocyanate groups). The bands between 2950 and 2850 cm^{-1} correspond to the asymmetric and symmetric C-H stretching vibrations respectively. The peak at 1710 cm^{-1} is due to the stretching vibrations of the C=O whilst the nearly overlapped bands between 1540 and 1517 cm^{-1} are attributed to the stretching and bending vibrations of the C-N and N-H of the urethane moieties, respectively. The bands at 1220 cm^{-1} and 1100 cm^{-1} are associated with the C-O stretching vibrations.

The small peak around 2270 cm^{-1} typical of residual NCO groups due to the excess of isocyanate used in the production of PUFs. Also, notice should be made that the presence of the filler content (EG, PCM and both) increased the 2270 cm^{-1} peak of the resulting composites. This may be attributed to at least two possibilities: *(i)* the hydroxyl groups on the surface of EG can alter the isocyanate index ($R_{NCO/OH}$) defined as the number of moles of NCO groups of the isocyanate per OH mole of the polyol thus affecting the consumption of NCO groups and *(ii)* the interference of the filler on the rate of the polymerization namely associated with changes in the rheological behavior of the reaction mixture.[53] Both possibilities may lead to a lower crosslinking density and affect the morphology of the foams as well as the thermal and mechanical properties of the ensuing composites. In fact, this can justify the differences on the structure and on the mechanical properties of the resulting foams.

4.4.4. Density

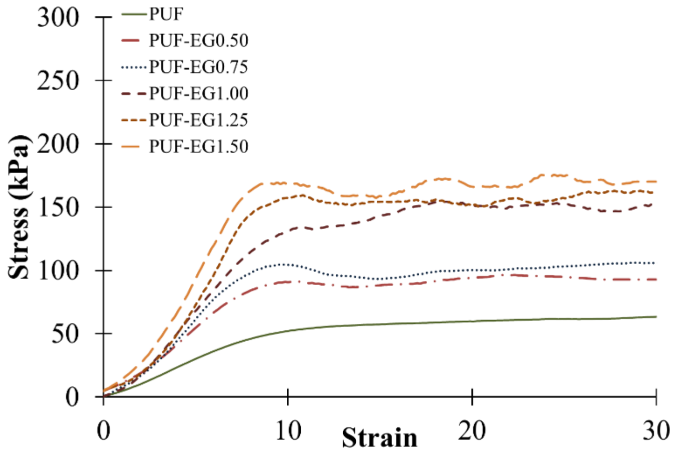
Density is an important property of foams because it affects their thermal and mechanical properties, among others. The density of foams depends on the quantity of gas released during the blowing agent/isocyanate reaction and on the quantity and nature of the surfactant. Also the incorporation of a filler (EG, PCMs and both) can affect foam density since they are a denser material and this effect can prevail over the other effects. Also it is quite common to find that the filler incorporation can affect foam density, due to the interference of the solid particles with the polymer and foaming reactions. The results summarized in Table 4. 3 confirm that the increase of density is related with the increase of the filler content and are in agreement with the results reported in the literature.[53,199,249]

Table 4. 3 - Properties of ensuring foams

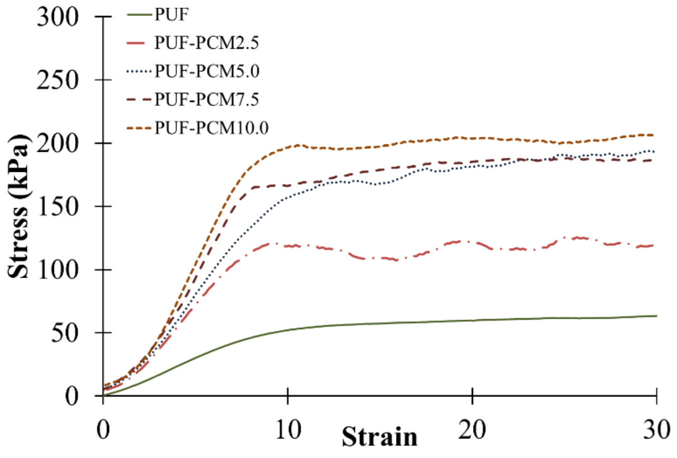
Sample	Density (kg/m^3)	Thermal conductivity (W/mk)	Young modulus (kPa)	Toughness (J/m^3)	Compressive stress $\sigma_{10\%}$ (kPa)
PUF	43.8 ± 1.4	0.035 ± 0.002	643 ± 27	15560 ± 1371	55 ± 2
PUF-EG0.50	74.0 ± 3.7	0.039 ± 0.001	1334 ± 43	29313 ± 1344	95 ± 4
PUF-EG0.75	84.2 ± 2.6	0.040 ± 0.001	1541 ± 59	34500 ± 2027	114 ± 7
PUF-EG1.00	92.9 ± 3.9	0.042 ± 0.001	1739 ± 74	40640 ± 1754	144 ± 8
PUF-EG1.25	84.8 ± 4.6	0.042 ± 0.001	1812 ± 66	42775 ± 2814	152 ± 8
PUF-EG1.50	99.3 ± 5.0	0.043 ± 0.002	1875 ± 89	45075 ± 4738	162 ± 8
PUF-PCM2.5	81.8 ± 2.9	0.036 ± 0.001	1729 ± 57	40280 ± 2132	144 ± 8
PUF-PCM5.0	91.9 ± 4.0	0.037 ± 0.002	2079 ± 91	47467 ± 2605	167 ± 11
PUF-PCM7.5	103.0 ± 6.0	0.038 ± 0.003	2312 ± 85	51960 ± 7412	175 ± 12
PUF-PCM10.0	118.2 ± 7.9	0.039 ± 0.001	2771 ± 117	59983 ± 3068	193 ± 12
PUF-EG1.00-PCM5.0	115.4 ± 5.8	0.044 ± 0.002	2765 ± 113	58856 ± 2163	193 ± 11

4.4.5. Mechanical properties

Compressive tests were performed to study the mechanical properties of the PUFs and in Figure 4. 7 and Table 4. 3, are presented the mechanical properties of PUFs.



(a)



(b)

Figure 4. 7 - Compressive stress-strain curves of EG composites (a) and PCMs composites (b)

The mechanical properties of PUFs depend primarily on the cells' morphology with the strength being higher in the direction of foam expansion. Thus, alterations on the ratio of height to diameter of cells will have a major impact. From Figure 4. 7 and Table 4. 3 it is clear that the Young modulus (*E*), toughness and compressive stress ($\sigma_{10\%}$) are related with the increase of EG content, as well as with the increase of PCMs content. The addition of fillers is known to have variable effects on the mechanical properties of the foams. Although it may have some positive effect, their use is generally associated with poor homogeneity which influence its mechanical properties [5,10]

4.4.6. Mechanical analysis

DMA experiments were carried out in order to obtain further information on the viscoelastic properties of PUFs. Materials such as PUFs typically exhibit two distinct types of behavior depending on the temperature. At low temperatures they exhibit the properties of a glass (high modulus) and at higher temperatures those of a rubber (low modulus). Figure

4. 8 displays the temperature dependence of the storage modulus and tan (δ) of PUF, PUF-EG1.00, PUF-PCM5.0 and PUF-EG1.00-PCM5.0.

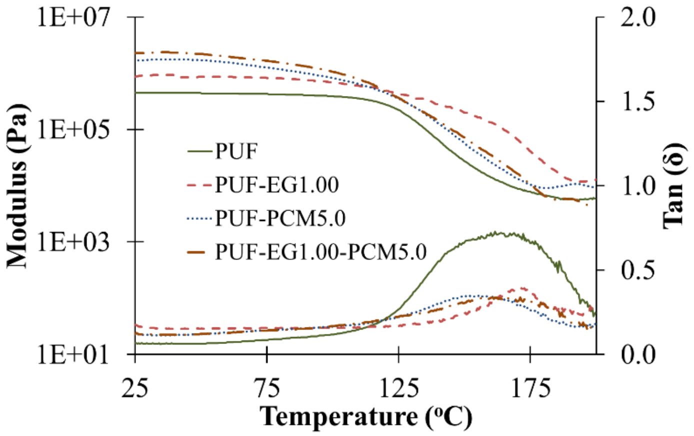
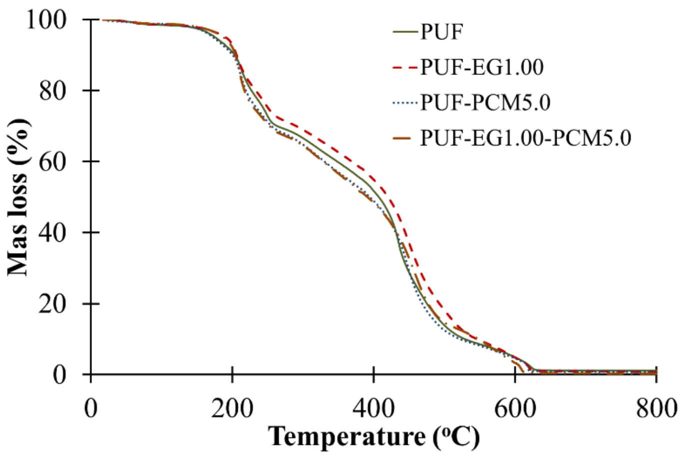


Figure 4. 8 - Temperature dependence of the storage modulus and tan (δ) of PUF, PUF-EG1.00, PUF-PCM5.0 and PUF-EG1.00-PCM5.0

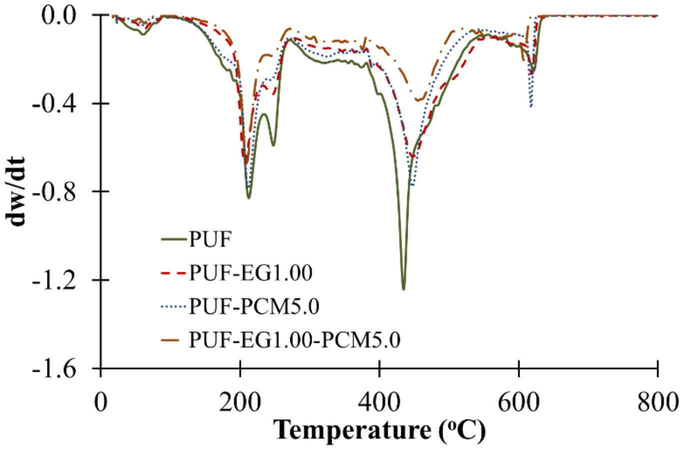
Below the glass transition temperature, PUF-EG1.00 and PUF-EG100-PCM5.0 have similar storage modulus around 1.9×10^6 Pa. Interestingly, in this type of dynamic mode of analyses, the behavior of PUF-EG1.00 and PUF-EG1.00-PCM5.0 is much more similar then that observed for the stress-strain tests.

4.4.7. Thermogravimetric analysis

The thermal degradation of PUFs is commonly characterized by the degradation of hard segments followed by the degradation of polyol segments and at lower temperatures the release of some volatile components.[227,228] The thermal degradation of these polymers was investigated by TGA and Figure 4. 9 displays the corresponding TGA curves of PUF, PUF-EG1.00, PUF-PCM5.0 and PUF-EG1.00-PCM5.0.



(a)



(b)

Figure 4. 9 - Thermal degradation (a) and dw/dt (b) of PUF, PUF-EG1.00, PUF-PCM5.0 and PUF-EG1.00-PCM5.0

As it can be seen from Figure 4. 9, the decomposition of PUFs is characterized by a very small weight loss at around 100 ºC due to the release of residual water, followed by two main decompositions steps: one around 210 ºC, related to the thermal decomposition of the hard segments (e.g. urethane groups) and a second, around 430 ºC related to the soft segments.[159] Despite of not following a trend, which is due to a possible heterogeneity of the foams, the results obtained are in agreement with those in the literature for similar materials.[228]

4.4.8. Differential scanning calorimetry analysis

In order to study the phase change behavior of the PCMs on the foams, PUFs filled with different PCMs content was measured by DSC. The DSC analyses were conducted on the base, middle and top of the foams, to evaluate the dispersion of the PCMs along the foams. DSC curves of PUFs are shown in Figure 4. 10.

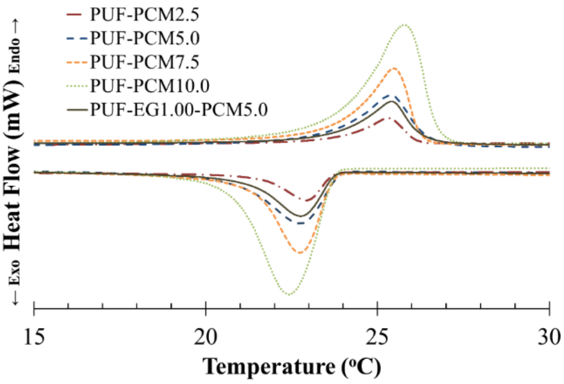


Figure 4. 10 - DSC curves of foams

Table 4. 4 - DSC results

Sample	T_1 (ºC)	T_2 (ºC)	T_3 (ºC)	Enthalpy (J/g)	% PCM
PCM	23.87	26.16	27.51	103.3891	100%
PUF-PCM2.5	23.95	25.31	26.16	2.5989 ± 0.1415	2.5% ± 0.1
PUF-PCM5.0	23.57	25.34	26.48	5.2420 ± 0.1266	5.1% ± 0.1
PUF-PCM7.5	23.77	25.41	26.13	7.6177 ± 0.2090	7.4% ± 0.2
PUF-PCM10.0	24.11	25.78	26.74	10.3811 ± 0.3448	10.0% ± 0.3
PUF-EG1.00-PCM-5.0	24.29	25.91	26.80	5.1499 ± 0.4821	5.0% ± 0.5

T_1 – initial temperature of the peak; T_2 – maximum temperature of the peak; T_3 – final temperature of the peak

The DSC analyses of foams revealed well-performed endothermic and exothermic enthalpy changes during heating and cooling between 15 and 30 ºC. the above summarizes the observed phase transition intervals as well as the enthalpies values during heating. In each case, the phase transition interval of the foams coincides with that of the PCM.

4.4.9. Numeric simulation

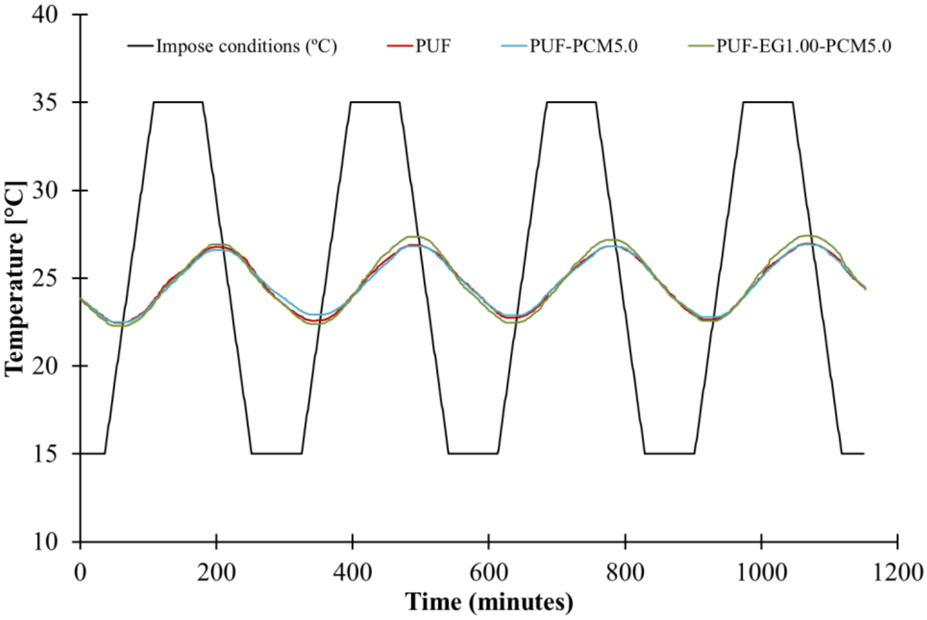


Figure 4. 11 - Temperature curve comparison (experimental data and numerical simulation) of PUFs

In Figure 4. 11 it is represented the indoor air temperatures using the PUF, PUF-PCM5.0 or PUF-EG1.00-PUF5.0 as thermal barrier material. From the results it was observed that the system responses for PUF and PUF-PCM5.0 are very similar. Moreover, the PUF-EG1.00-PCM-5.0 was not able to reduce the indoor temperature at the higher temperatures neither increase the indoor temperature at the lower temperatures when compared with the PUF or PUF-PCM5.0. This may be due to the fact that filling the PUF with PCM and/or EG, both thermal conductivity and density of the materials increase with reduce their capability to absorb energy.

4.5. Conclusions

In the present study ecofriendly PUFs were produced from CG which was used directly, without any purification step. Also it was studied the enhancement of the thermal properties of the PUFs by adding PCMs and EG. Besides of the improvement of the mechanical and thermal properties of the foams, no improvement in the indoor temperature was reached when PCMs and/or EG were used, possibly due to the higher thermal conductivity and density of the composites.

5. Improvement of the reaction to fire of CG derived foams

This chapter was presented as oral communication (N. V. Gama, B. Godinho, R. Silva, A. Barros-Timmons, A. Ferreira, "Flame retardant properties of crude glycerol polyurethane foams filled with expanded graphite"), at the ICMTech conference, in Delhi, in 2016, which was awarded with the Young Scientist Award of year 2016, attributed by the International Association of Advanced Materials. Also this chapter was submitted for publication in the journal Polymer Degradation and Stability.

5.1. Abstract

Rigid PUFs obtained from renewable ressources are getting considerable attention. However, their reaction to fire have not received as much attention despite of their increasing relevance. In this study the reaction to fire of composite PUFs derived from CG was studied and the effect of using EG as flame retardant evaluated. The fire performance of the PUF and EG/PUF composites has been investigated and the results obtained showed that the fire behavior of composite foams containing as little as 5 wt% of EG is significantly improved. Moreover the use of Infrared thermography as a function of time has proven that when EG is used the combustion stops suddenly suggesting that EG acts like a flame extinguisher. The results obtained have proven the suitability of CG for the production of PUFs and that the addition of EG considerably improves the reaction to fire of composite foams.

Keywords: Polyurethanes; Porous Materials; Composites; Flame Retardance; Degradation

5.2. Introduction

PUFs, like other polymers, rely on fossil feedstock’s, because its two main reactants (the polyol and the isocyanate) derive from petroleum feedstock´s. However, the increasing concern over environmental impact and scarcity of petroleum, has motivated the development of PUFs from bio and renewable raw materials.[47] In fact, extensive research has been concentrating on developing, bio-based polyols from renewable sources, such as biomass residues, vegetable oils or industrial by-products.[51,53,54,90,97,220,251] The resulting foams are mainly rigid due to the small chain length of the polyols, high cross linking density associated with high functionality and in some cases the presence of rigid groups such as aromatic rings. Therefore, this type of materials is generally used as structural and thermal insulation materials for construction.[252]

Rigid PUFs as well as most organic materials burn very easily. Despite of that, for many years the fire performances of PUFs were suitable, but nowadays materials have to meet ever more stringent requirements due to the greater attention paid to fire safety and improved fire performances are thus required.

During combustion, PUFs generate highly toxic smoke, especially CO and hydrogen cyanide. The inhalation of these gases causes severe health problems or even death. Also, during a fire, there is a dramatic increase of temperature which leads to the decomposition of PUFs affording small molecules in the gaseous phase. The mixture of these small molecules with air forms a flammable mixture. In other words, when the concentration of this mixture and temperature cross the flammability limit, the material starts to burn.[190]

The behavior of a material with fire, can be classified by: (*i*) resistance to fire and (*ii*) reaction to fire. The fire resistance provides information about how well a building element, such as a wall, floor, door, etc, can maintain its properties when exposed to a fire. It is only related with what happens after flashover. The reaction to fire is related with the instant after the beginning of a fire, its propensity to ignite or feed a fire. This behavior is assessed on the basis of standardized tests and described in a Euroclass classification.

As mentioned before, as a result of the increasing awareness of public opinion, the flammability properties of PUFs need be improved and this can be achieved by the incorporation of flame retardants.[190] The flame retardance mechanisms are physical and/or chemical thus, the use of different types of flame retardant can significantly change the flame retardance mechanisms.

Flame retardants can be used as additives or as reactives in order to interfere with combustion during different stages such as heating, decomposition, ignition, or flame spread. Halogenated paraffins and phosphorus containing compounds are commonly used as flame retardants. The former may not be very compatible with the PUFs and for that reason may jeopardize the mechanical properties of the materials besides releasing irritant acids. The latter, being a reactive type flame retardant can react with functional groups of PUFs. They act as char-forming agents, reducing the generation of flammable gases.[190] Reactive type flame retardants have the advantages of (*i*) increasing compatibility between polymer, (*ii*) not degrading the mechanical properties of the PU, (*iii*) possessing better compatibility as the flame retardant group is a part of the binder and (*iv*) using small amount or low concentration for the enhancement of fire-retardancy.[190]

A very distinct type of flame retardants are inorganic fillers. These materials produce a stable organic–inorganic interface, which reduces the concentration of decomposition gases and increases the diffusion path barrier of the volatiles produced during the degradation process.[190] Nowadays EG is widely used as flame retardant in PUFs. Recently, A. Lorenzetti *et al.* [253] reported the effect of expansion volume and of intercalants on the flame retardancy of EG in PUF and concluded that the expansion volume of EG does not seem to have a major influence on the reaction to fire of this type of materials. Yet, the nature of EG intercalants does affect the fire retardancy properties of PUFs, with sulfur based intercalants ones being more efficient than phosphorous ones.

Polyols from renewable resources commonly used in the production of PUFs are obtained from different vegetable oils such as rapeseed oil, castor oil, palm oil or soybean oil (e.g., BASF castor oil-based Balance™, Cargill soybean-based BiOH™, and Dow soybean-based Renuva™).[254] Most of them are already used at industrial level but the production of these polyols is competing with the production of food. In that sense, CG which is a byproduct of the biodiesel production, has received considerable attention.[52,54,155] Aleksander Hejna *et al.* [255] reported the reaction to fire of PUFs derived from CG, however the CG was used as polymerization reactant, together with castor oil to produce a bio-based polyol. Also the synthesized bio-based polyol was used as partial substitution (0–70 wt.%) of petrochemical polyol in the production of PUFs.

Hence, to the best of our knowledge, this is the first report of PUFs derived from the direct use of unrefined CG evaluating its reaction to fire and improving it via the addition of EG and the results obtained showed that the fire behavior of PUFs containing 5 wt% of EG is significantly improved.

5.3. Experimental

5.3.1. Materials

The foams studied were produced from the reaction between CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. CG sample was kindly supplied by Bioportdiesel and had a water content of 1.6 ± 0.01, an acid value (*AV*) of 23.1 ± 0.2 $mg_{KOH}.g^{-1}$ and an hydroxyl number (OH_{number}) of 399.0 ± 4.7 $mg_{KOH}.g^{-1}$. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% and a functionality of 2.7 was kindly supplied by Dow Chemicals. Tegostab B8404, a polyether-modified polysiloxane was used as silicone surfactant and was supplied by Evonik. Polycat 34, a tertiary amine was used as catalyst and supplied by Air Products. As blowing agent, distilled water was used. EG (EG GHL PX 95) was supplied by LUH and had a thermal conductivity of 0.290 $mWm^{-1}K^{-1}$ (at room temperature) and a density of 0.5436 $g.cm^{-3}$. A detailed characterization of the EG sample used has been provided in previous reports [53] including the evaluation of its reactivity towards the isocyanate using XPS analysis, Fourier transform Infrared (FTIR), FT-Raman spectroscopy, X-ray diffraction and thermogravimetric analysis (TGA).

5.3.2. Characterization of crude glycerol

The water content, acid value (*AV*) and hydroxyl number (OH_{number}) of the CG were determined according to the procedures describedin Chapter 1.

5.3.3. Production of PUFs

The polyol component and the corresponding amounts of catalyst (3 parts per 100 parts of polyol w/w), surfactant (4 parts per 100 parts of polyol w/w) and blowing agent (*6 - x* parts per 100 parts of polyol w/w, *x* being to the amount of water present in the polyol), were placed in a polypropylene cup and homogenized using an mechanical stirrer for *ca.* 10 seconds at 700 rpm. As referred above, notice should be made that the amounts of water present in the polyols were subtracted to the amounts of blowing agent added. Next, different amounts of EG (from 5% up to 20% (w/w)) were added and the mixture blended again. Finally, the appropriate amount of isocyanate to obtain a $R_{NCO/OH}$=1.10 (ratio between NCO groups of isocyanate and OH groups) was added and the mixture homogenized again. The $R_{NCO/OH}$ used in the PUFs production was determined using Eq. (11).

$$R_{NCO/OH} = (m_{ISO} \times \%_{NCO}/M_{NCO})/(m_{polyol} \times (OH_{number} + AV)/M_{KOH} + (m_{H_2o} + m_{BA}) \times Eq_{H_2o})$$

Eq. (11)

Where $R_{NCO/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH moles of each polyol and water, m_{iso} is the mass (g) of isocyanate, *%NCO* is the quantity of NCO groups in the isocyanate (31.1%) and M_{NCO} is the molecular weight of NCO group. m_{polyol} is the mass (g) of each polyol, OH_{number} and *AV* are the hydroxyl number and the acid value of each polyol respectively ($mg_{KOH}.g^{-1}$). M_{KOH} is the molecular weight of

KOH. m_{H2O} is the mass of water present in each polyol, while m_{BA} is the mass of blowing agent (water) added. Finally, Eq_{H2O} is the equivalent of OH groups present in the water.

The foams were obtained by free expansion in the cup mold at room temperature and the formulations are listed in Table 5. 1.

Table 5. 1 - Foam formulations

Sample code [a]	CG	Isocyanate (PHP)	Catalyst (PHP)	Surfactant (PHP)	Blowing Agent (PHP)	EG
PUF-EG0	100	209	3	4	4.4	0
PUF-EG5	100	209	3	4	4.4	17
PUF-EG10	100	209	3	4	4.4	35
PUF-EG15	100	209	3	4	4.4	56
PUF-EG20	100	209	3	4	4.4	80

[a] *Sample Code (PUF-EGX): X - wt% of EG*

5.3.4. Characterization of PUFs

Fourier Transform Infrared Spectroscopy (FTIR), density, Scanning Electron Microscopy (SEM), mechanical essays, Dynamic Mechanical Analyses (DMA) using the material pocket accessory and Thermogravimetric Analysis (TGA) were determined according to Chapter 1.

FT-Raman spectra were recorded in a Jobin Yvon TH800 (Horiba) Raman spectrophotometer using a 100× objective. The spectral range was 1200–3200 cm^{-1}.

XRD patterns of EG and EG-MDI were obtained using a PANalitycal Empyrean diffractometer operating with Cu Kα radiation. The scattered radiation was detected in the angular range (2θ) from 0^o to 60^o.

The thermal conductivity measurements were performed using the Gustafsson Probe method (or Hot Disk) with the Thermal Constant Analyser TPS 2500S.[256] This transient method uses an electrically conducting pattern (Nickel) element acting both as a temperature sensor and heat source, insulated with two thin layers of Kapton (70 µm). The TPS element is assembled between two samples of similar characteristics with both faces in contact with the sensor surface. For isotropic samples, the Hot Disk method allows the determination of the thermal conductivity, thermal diffusivity and specific heat. The Hot Disk method is an international standard for measuring thermal conductivity and thermal diffusivity with the designation ISO 22007-2.

Infrared Thermography was used to map dynamic heat transfer processes in real-time. Samples with dimensions of 10x10x10 mm were ignited with a Bunsen burner inside of a fume hood. After 4s the flame source was removed and images of the sides of the burning specimens were recorder using a FLIR SC5650 camera with a Stirling cycle cooled Indium Antimonide detector, 25mK sensitivity, 640x512 resolution and was used at a 25 Hz windowed frame-rate.

The fire behavior of three samples of each foams were analyzed using a cone calorimeter apparatus according with ISO 5660 [257] at the Department of Applied Science and Technology (DISAT), Alessandria Section – Politecnico di Torino. The cone calorimeter apparatus exposes a small square horizontal test specimen (100x100x20 mm) to a preset heat flux (in our trials 50 kWm^{-2}), in the presence of an air flux (24 ls^{-1}) as in then ignited by electric spark. The fire effluent passes through a duct, containing a sensor which permits the determination of the rate of heat release (*RHR*) (by oxygen consumption) while CO and CO_2 production, expressed as kg of gas developed/kg of material combusted, is determined by infrared spectroscopic techniques. The test stops when the flame extinguishes. During the test several parameters can be measured, such as: *RHR* (kW.m^{-2}); effective heat of combustion (*EHC*) (MJ.kg^{-1}); mass loss (g.s^{-1}); residual mass (%), carbon monoxide and dioxide production (kg.kg^{-1}) and specific extinction area (*SEA*) (m^{2}.kg^{-1}). The parameters were recorded during time. After data elaboration, it is possible to obtain the peak and the mean value for each parameter during test (except for mass loss). Often, the value that is considered for analyzing fire behavior is the peak one, as it represents the worst situation in a real fire scenario.

5.4. Results and discussion

PUFs are widely used as thermal insulation materials for construction and in previous reports, the suitability of renewable feedstocks for the production of thermal insulation foams has been reported.[51,54,258,259] However, their reaction to fire have not received as much attention. Hence, in the present work, the reaction to fire of CG derived PUFs are improved by the addition of EG.

5.4.1. Monitoring of the reaction

FTIR spectrophotometry was used to monitor the formation of the urethane linkages, as a result of the reaction between the NCO groups of the isocyanate and OH groups of the CG as well as to monitor the extent of this reaction. All normalized FTIR spectra are presented in Figure 5. 1.

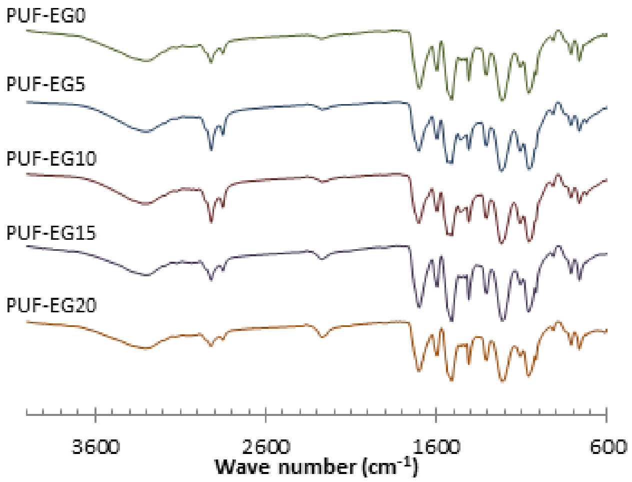
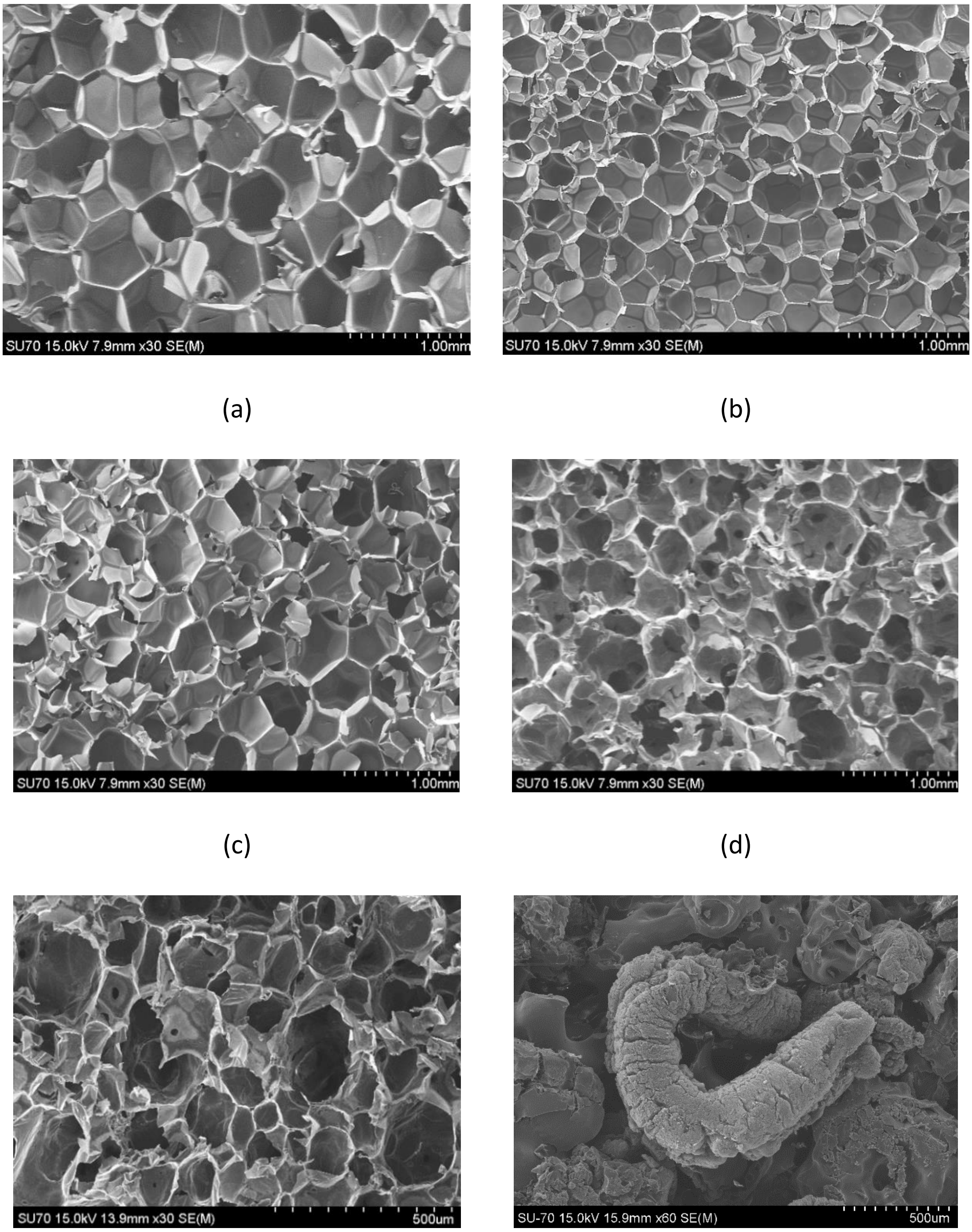


Figure 5. 1 - Normalized FTIR spectra of PUF and PUF-EG composites

The normalized FTIR spectra of all samples present very similar profiles. In the two typical spectral regions of the urethane groups, a peak at 1710 cm^{-1} due to the stretching vibrations of the C=O of the urethane and ester groups of the polyol is present. Since isocyanate used reacts with water which was used as blowing agent, the presence of the peak at 1650 cm^{-1} typical of urea groups is also detected. The following region is associated with the nearly overlapped bands between 1540 and 1517 cm^{-1}, attributed to the free N-H absorption and to N-H groups which are hydrogen-bonded with carbonyl groups, respectively. Worthy of notice is the fact that with the increase of the EG amount, the small peak around 2270 cm^{-1}, typical of the stretching vibration of residual NCO groups, becomes more evident. As discussed in previous reports [53] this may be attributed to at least two possibilities: *(i)* the hydroxyl groups on the surface of EG can alter the isocyanate index ($R_{NCO/OH}$) defined as the number of moles of NCO groups of the isocyanate per OH mole of the polyol (which has been corrected for the presence of water but not for the presence of fillers) thus affecting the consumption of NCO groups and *(ii)* the interference of the EG on the rate of the polymerization namely associated with changes in the rheological behavior of the reaction mixture and/or coupling of EG surface groups with either the isocyanate, the polyol and/or the water used as blowing agent [260].

5.4.2. Morphology

SEM analysis is an important and versatile tool to inspect the foam structure. During mixing, air bubbles are usually introduced in the reaction mixture and act as nucleation sites for the blowing gas generated from the reaction between isocyanate and blowing agent. The bubbles grow resulting in a closely packed network of bubbles responsible for the typical cellular structure of PUFs.[218] The cell structures of PUF-EG composites are presented in Figure 5. 2.



(a) (b)

(c) (d)

(e) (f)

Figure 5. 2 - SEM images of PUF-EG0 (a), PUF-EG5 (b), PUF-EG10 (c), PUF-EG15 (d), PUF-EG20 (e) and the “worm” like structure of the burnt EG (f)

From Figure 5. 2 it is clear that the increase of the EG content results in poor homogeneity, especially for higher amounts of EG. The irregularity of the cellular structure is related to the fact that the EG content can affect the foaming process due to interactions between the polymer matrix and fillers during bubble nucleation, cell growth, and stabilization stages.[248] Furthermore, the aspect ratio of EG is also known to influence the shape of the cells and induce cell rupture. As the percentage of EG increases local stresses and/or irregular foam growth occur which is clearly observed in Figure 5. 2 (e). Similar cases have been reported by others in the literature.[199,261] Also, the heterogeneity of the cells size increases, and it can be seen by the standard deviation of average cell size listed in Table 5. 2. Since the morphology has a paramount importance on the properties of the foams, these observations are expected to have significant effect on the properties of the foams. Table 5. 2 summarizes the physical properties of PUF-EG composites prepared.

Table 5. 2 - Physical properties of PUF/EG composites

PUF	Density (kg.m^{-3})	Average cell size (µm)	Young's modulus (kPa)	Toughness (J.m^{-3})	Compressive stress 10% (kPa)	Tg (ºC)
PUF-EG0	44.5 ± 2.8	202.9 ± 8.7	620 ± 12	15629 ± 2716	46 ± 4	118.6
PUF-EG5	57.8 ± 3.1	195.7 ± 10.4	1858 ± 57	25467 ± 2715	128 ± 9	123.1
PUF-EG10	63.4 ± 3.6	186.4 ± 18.5	2270 ± 74	29883 ± 3010	140 ± 13	131.3
PUF-EG15	69.5 ± 4.0	178.8 ± 28.5	2581 ± 60	33857 ± 3678	149 ± 11	136.6
PUF-EG20	73.9 ± 4.3	152.6 ± 38.6	2864 ± 72	37283 ± 4318	163 ± 11	143.3

5.4.3. Density

The density of PUFs depends on the quantity of gas released during the blowing agent/isocyanate reaction and on the quantity and nature of the surfactant used, among others. However, the incorporation of fillers has a significant effect since addition of a more dense material to the foam can prevail over the other effects. Moreover, incorporation of fillers may also affects foam's density due to *(i)* the interference of the solid particles with the reaction between NCO groups with OH groups, and *(ii)* their influence on the foaming process, as referred above. The results obtained for the different samples prepared are summarized in Table 5. 2 and confirm that the increase of EG load is associated with an increase in density. This is also in agreement with the results reported in the literature.[199,249]

5.4.4. Mechanical properties

Compressive tests were performed to study the mechanical properties of PUFs and assess the effect that EG has on the stiffness of the foams. Figure 5. 3 illustrates the compressive stress-strain plots of the PUFs prepared and in Table 5. 2 the values determined for the Young's modulus, toughness and compressive stress are summarized.

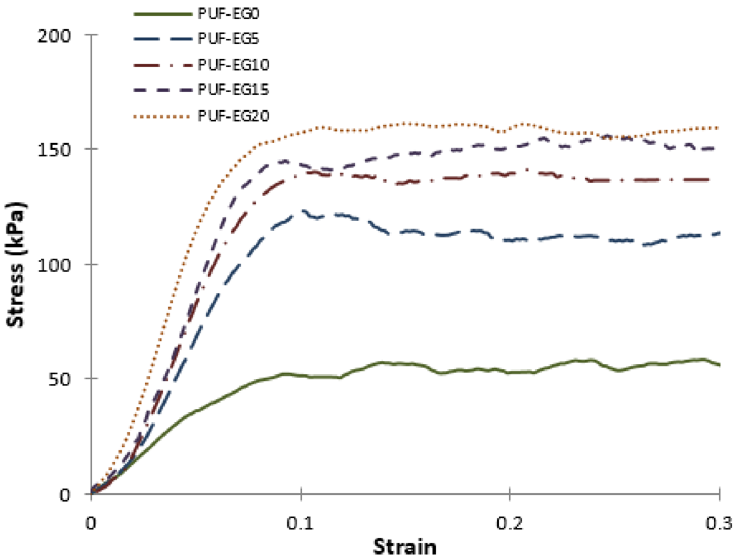


Figure 5. 3 - Compressive stress-strain curves of PUFs

The mechanical properties of PUFs depend primarily on the cells' morphology with the strength being higher in the direction of foam expansion. Thus, alterations on the ratio of height to diameter of cells will have a major impact. On the other hand, addition of EG to

PUFs is known to have variable effects depending on the percentage of loading, on the size of particles and, whether the fillers are partially incorporated in the cell walls, or between them. Furthermore, as discussed previously, the reaction between the isocyanate and the functional groups on the EG surface and lead to a reduction of crosslinking density of the polymer matrix, which affects the mechanical properties of the ensuing composites. The results summarized in Figure 5. 3 and Table 5. 2, show that the Young's modulus (E), toughness and compressive stress ($\sigma_{10\%}$) are linearly related to the increase of EG.

5.4.5. Dynamic Mechanical Analysis

DMA measurements were carried out in order to determine the glass transition (*Tg*) of composites foams. To be sure that the *Tg* values were not affected by possible heterogeneities of the samples, analyses of powdered samples were also carried out using the material pocket accessory of the DMA instrument. From Table 5. 2 it is clear that the *Tg* values of PUFs increase with the increase of the filler content. The *Tg* values of composites and nanosystems have been widely investigated and different effects on the *Tg* have reported [261] as it depends on variety of issues. As shown in Table 5. 2, the PUFs filled with EG showed higher *Tg* than the pristine PUF, due to the rigid filler system which limited the mobility of the polymer chains. Similar results are reported in literature. [194]

5.4.6. Thermal conductivity

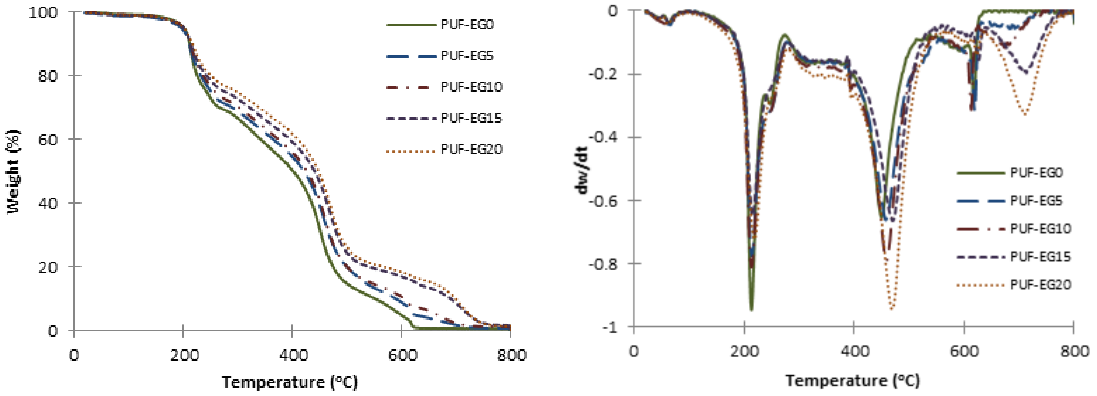
Generally, the thermal conductivity (*k*) is related to the foams density, the ratio of open/closed cells and the thermal conductivity of the gas used as blowing agent. Whilst the whole foam only contains a small fraction of PU, and the *k* value of the polymer is much higher than that of the blowing agent, higher density foams have higher thermal conductivity.[167] Yet, in the case of PUF/EG composites, as EG itself has a high thermal conductivity its presence is expected to increase the PUFs thermal conductivity. In fact, the thermal conductivity of this type of composites is governed by the transport of phonons whose transport is favored by the larger grain and crystallite size of bigger graphite flakes as the interface is reduced [262]. Therefore, as higher percentages of EG are used, aggregates may become larger, facilitating the transport of phonons and consequently the thermal conductivity increases. As regards the role of EG as a fire retardant, what actually is of interest is its thermal barrier effect, i.e. the thermal diffusivity of the material which is the rate of transfer of heat of a material from the hot side to the cold side and which is calculated dividing the thermal conductivity by density and specific heat capacity at constant pressure [263]. Since the addition of EG increases the specific heat of the material and the density (see Table 5. 2 and Table 5. 3), the thermal diffusivity of the composites decreases as the load of EG increases. Therefore, the heat transfer rate from the hot side to the cold side drops when higher loadings of EG are used which helps to prevent combustion as will be discussed next.

Table 5. 3 - Thermal properties of PUFs/EG composites

PUF	Thermal conductivity ($Wm^{-1}K^{-1}$)	Thermal diffusivity (mm^2s^{-1})	Specific heat ($MJm^{-3}K^{-1}$)
PUF-EG0	0.039	0.428	0.097
PUF-EG5	0.047	0.336	0.148
PUF-EG10	0.049	0.321	0.154
PUF-EG15	0.053	0.309	0.171
PUF-EG20	0.081	0.214	0.380

5.4.7. Thermogravimetric analysis

As mentioned earlier, one of the limitations of polymeric materials is their poor thermal stability at high temperatures and EG is frequently used to minimize this and confer fire retardant properties.[264] The thermal degradation of these composites was investigated by TGA under oxygen atmosphere and compared with the results obtained for EG and neat PUF.



(a) (b)

Figure 5. 4 - Thermal degradation (a) and dw/dt (b) of PUFs

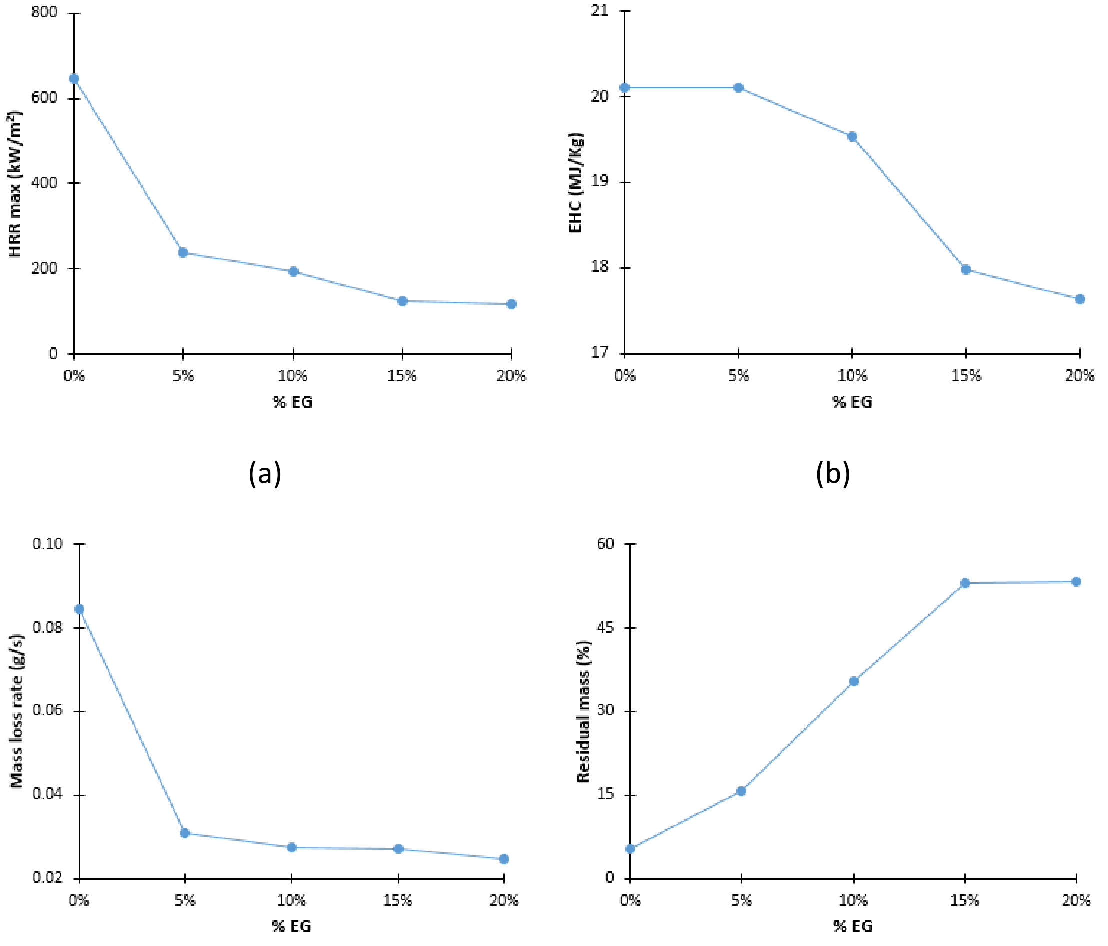
As expected the decomposition profiles observed are typical of PUFs which are characterized by two main decompositions steps: one around 180 ºC, related to the thermal decomposition of the hard segments (e.g. urethane groups) and gases released by EG, and a second around 460 ºC related to the soft segments.[159,227,228]. From TGA, it was observed that the presence of EG reduced the weight loss of PUFs in the initial stage of degradation. At 215 ºC, the weight loss of the neat foam was 13.9%, while the weight loss of PUF-EG20 was only 9.8%. The reduction of weight loss is in accordance with the increase of the residual mass results of the cone calorimetric tests, as will be discussed later. Also, Figure 5. 4 (a) reveals small differences in the second decomposition step associated with the soft segments. The slight differences detected regarding the rate of decomposition of the soft segments for the different loads of EG, can be ascribed to the poor dispersion of the fillers and changes of the crosslinking density.[190]

5.4.8. Reaction to fire

The reaction to fire of the foams were evaluated my means of cone calorimeter analysis and the obtained results are presented in Figure 5. 5 and Table 5. 4.

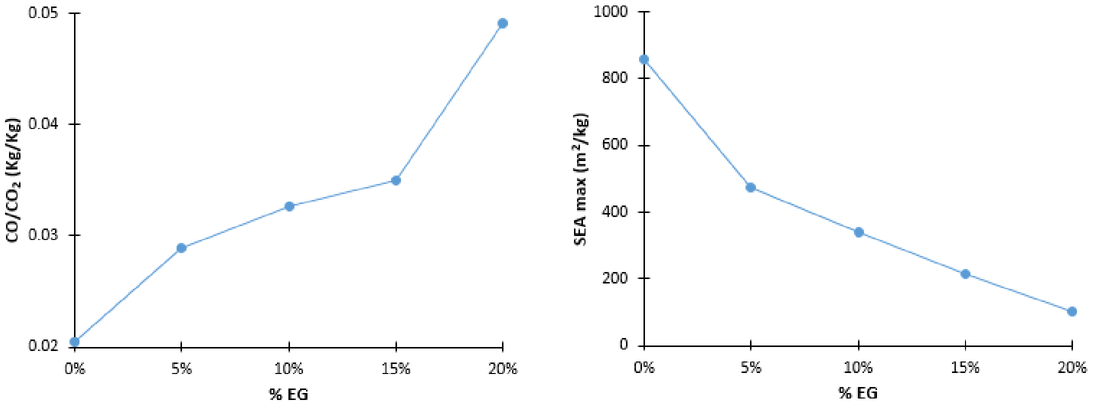
Table 5. 4 – Reaction to fire values of PUFs/EG composites

Sample	HRR max (kWm^{-2})	CO/CO_2 ($KgKg^{-1}$)	EHC ($MJKg^{-1}$)	Mass loss rate ($gs^{-1}m^{-2}$)	SEA max (m^2kg^{-1})	Residual mass (%)
PUF-EG0	645.8 ± 46.0	0.020 ± 0.001	20.1 ± 0.3	0.084 ± 0.011	856.8 ± 23.9	5.3 ± 0.5
PUF-EG5	238.2 ± 21.9	0.029 ± 0.001	20.1 ± 0.3	0.031 ± 0.003	471.6 ± 123.0	15.7 ± 3.3
PUF-EG10	194.9 ± 17.7	0.033 ± 0.007	19.5 ± 0.1	0.027 ± 0.001	339.9 ± 58.8	35.3 ± 6.8
PUF-EG15	125.0 ± 9.5	0.035 ± 0.001	18.0 ± 0.4	0.027 ± 0.001	213.8 ± 6.2	53.0 ± 0.8
PUF-EG20	116.2 ± 1.3	0.049 ± 0.002	17.6 ± 0.1	0.025 ± 0.001	102.4 ± 19.7	53.3 ± 2.9



(a) (b)

(c) (d)



(e) (f)

Figure 5. 5 - HRR max (a), EHC (b), mass loss rate (c), residual mass (d), CO/CO2 ratio (e) and SEA max (f)

One of the most important reaction to fire parameters is the heat release rate (*HRR*). It represents a quantity of heat generated per unit area and time, and is related with the flashover phenomena in a real fire situation.[196] From the results presented in Table 5. 4 and Figure 5. 5 (a), it can be seen that this parameter dropped significantly with the presence of the flame retardant. In fact, the *HRR* value of PUF-EG5 is 63% lower when compared with the pristine foam. When a sample is ignited, heat is generated so *HRR* is an index of the extent of fire.[197] From the videos, it can be seen that when EG is used, the flame stops from the moment the ignition source is removed, preventing the complete combustion of the foams. In other words, even though the exterior of the material is burned, the interior remains intact (see Figure 5. 9). The same observations were reported by A. Lorenzetti *et al.* [253] From the study of the effect of expansion volume and intercalants on the flame retardancy of EG in PUFs, it was reported that the decrease of the *HRR* is associated with the heat shield formed by the expantion of the EG due to: (*i*) the gases which are released from the redox reaction (explained below) of EG dilute the flammable gases, suffocating the flame; and (*ii*) the decomposition (endothermic process) absorbs the heat released.

The effective heat of combustion (*EHC*), which is the ratio of *HRR* to mass loss rate, discloses the degree of burning of volatile gases in gas-phase flame during combustion [198]. *EHC* provides an insight of the mechanism of flame retardants and as it can be seen in Table 5. 4 and Figure 5. 5 (b), the presence of EG is associated with a reduction of the *EHC* value, even though the mass loss also decreases with the presence of EG (see TGA results). This means that the presence of EG prevents the combustion and the release of heat when the matrix is decomposed into the gas products. Jarosinski *et al.*, have attributed this to the fact that some products released by the flame retardant could quench radicals derived from the matrix and prevent the combustion of original ignitable components.[265]

The char layer produced from the EG, being a thermal barrier as well as an oxygen barrier, prevents further decomposition of the materials. Therefore, due to this protection effect, increasing the amount of EG leads to a reduction of the rate of mass loss (Table 5. 4 and Figure 5. 5 (c)), and subsequently the residual mass of the PUFs after burned increased (Table 5. 4 and Figure 5. 5 (d)). This result is in agreement with the higher percentage of resiude registered in the studies by TGA, when higher loads of EG were used (Figure 5. 4 (a)) as well as the thermal diffusivity data presented in Table 5. 3. Nevertheless, the role of EG as flame retardant is also associated with its ability to expand forming the so called ‘‘worm’’ like structure (see Figure 5. 2 (f) and Figure 5. 8). The expansion of this filler suffocates the flame and the compact char layer formed limits the heat and mass transfer from the polymer to the heat source. According to M. Modesti *et al.* [266], this expansion is due to a redox process between H_2SO_4 (present within the graphite layers) and the inner graphite surface that generates gases according to the reaction:

$$C + 2H_2SO_4 \rightarrow CO_2 + 2H_2O + 2SO_2$$

In fact, the gases released can increase the volume of the materials by about 100 times. This structure modification was confirmed by FT-Raman and XRD analyses (see Figure 5. 6 and Figure 5. 7).

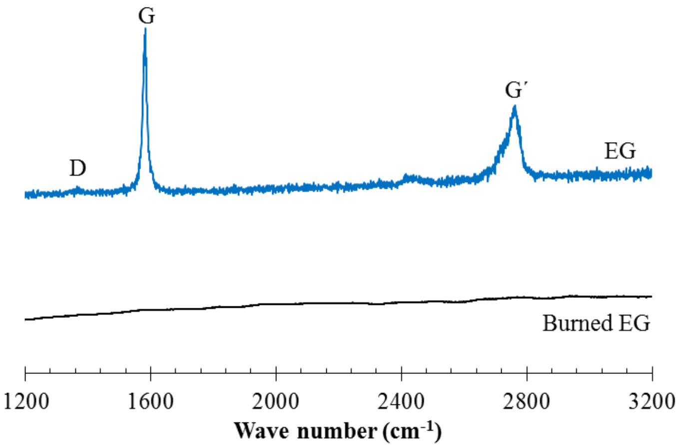


Figure 5. 6 - FT-Raman spectra of EG and burned EG

From Figure 5. 6, it can be seen the typical FT-Raman spectra of EG. The *D* band appears at 1370 cm^{-1}, the *G* band appears at 1580 cm^{-1} and the *G´* band at 2760 cm^{-1}. However, all these bands disappear in the Burned EG sample, meaning that the structure of EG was severally modify in the burning process.

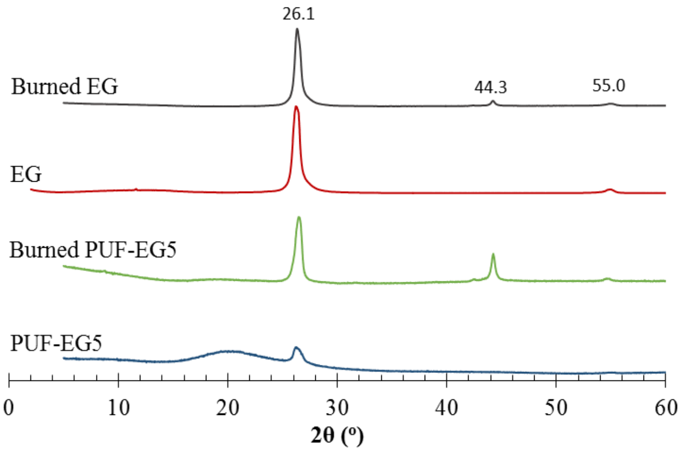


Figure 5. 7 - XRD patterns of PUF-EG5, burned PUF-EG5, EG and burned EG

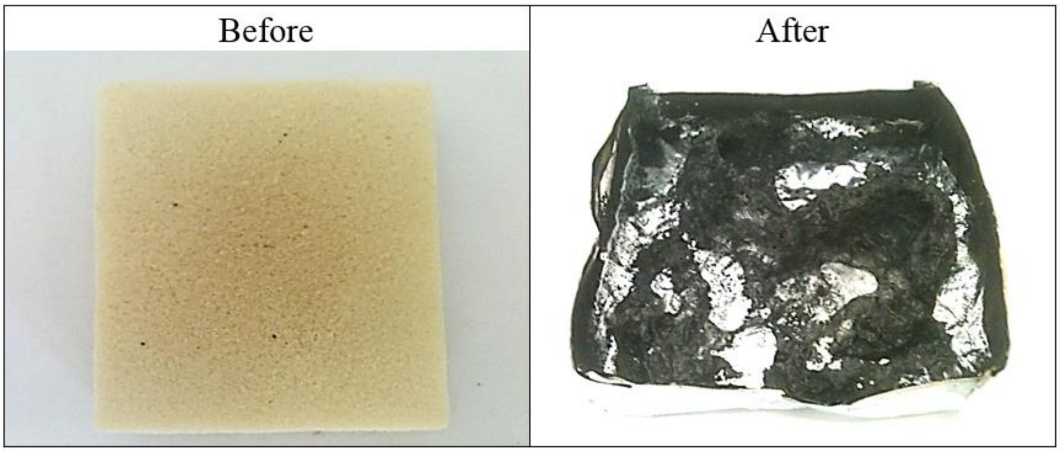
From the results presented in Figure 5. 7, it can be again observed that the burning process significantly modify the structure of EG. The PUF-EG5 and EG samples present the peak at 26.1^o, however when these samples were burned, in the resulting XRD patterns, it is observed the peak at 44.3^o. As mentioned before, in the burning of EG, occurs a redox reaction which is responsible for the expansion of EG and this may have two different effects on the structure of the EG: (*i*) the expansion may led to the structure planes to slipped out of alignment [267] and (*ii*) since the reaction may introduce oxygen groups in the EG structure, this may led change the crystalline structure.[268] Both may be responsible for turbostratic disorder (significant change of the crystalline structure), which is in agreement with the FT-Raman results.

The CO/CO_2 weight ratio can be taken as an index of combustion completeness, as well as of smoke toxicity as it is well known that compounds deriving by incomplete combustion are more toxic than those deriving by complete one.[199] In Table 5. 4 and Figure 5. 5 (e) the variation of CO/CO_2 weight ratio as a function of EG loading indicates that the higher the percentage of EG the higher the toxicity of the smoke. This is due to the physical barrier effect of the char layer formed which thwarts the oxygen diffusion and favors the development of products of incomplete combustion, like CO. Nevertheless, the CO/CO_2 values obtained for the neat and PUF-EG05 foams, are lower then PUFs produced from petroleum feedstock, tested under the same conditions.[199]

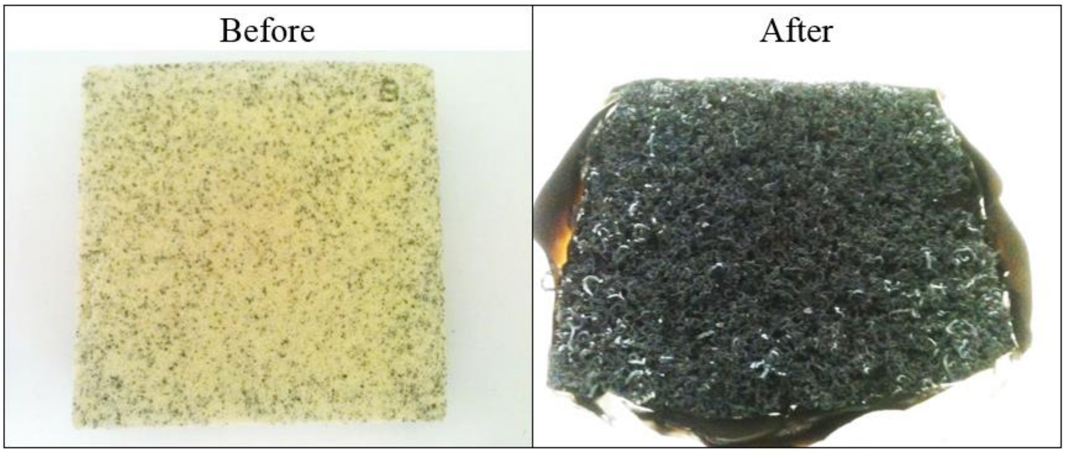
The specific extinction area (*SEA*) is a measure of smoke density and its value should be as low as possible so that people can more easily escape from a fire situation [196]. From the results presented in the Table 5. 4 and Figure 5. 5 (f), it can be seen that the presence of the flame retardant, significantly decreased the values of this parameter, meaning that it has an important role in the condensed phase.

Considering the distinct effect that EG loadings have on the different reaction to fire parameters, within the range studied, 5 wt% was considered the best compromise. This percentage of filler ensures a significant reduction of the maxium heat released and of mass loss when compared to the unfilled PUF and the lowest toxicity of smoke when compared to higher loading tested. Moreover, the use of 5 wt% EG already has a good impact on the mechanical properties of the ensuing composite PUF and minimal impact on the cellular structure.

In Figure 5. 8 is presented the PUFs before and after the cone calorimetric analysis.



(a)



(b)

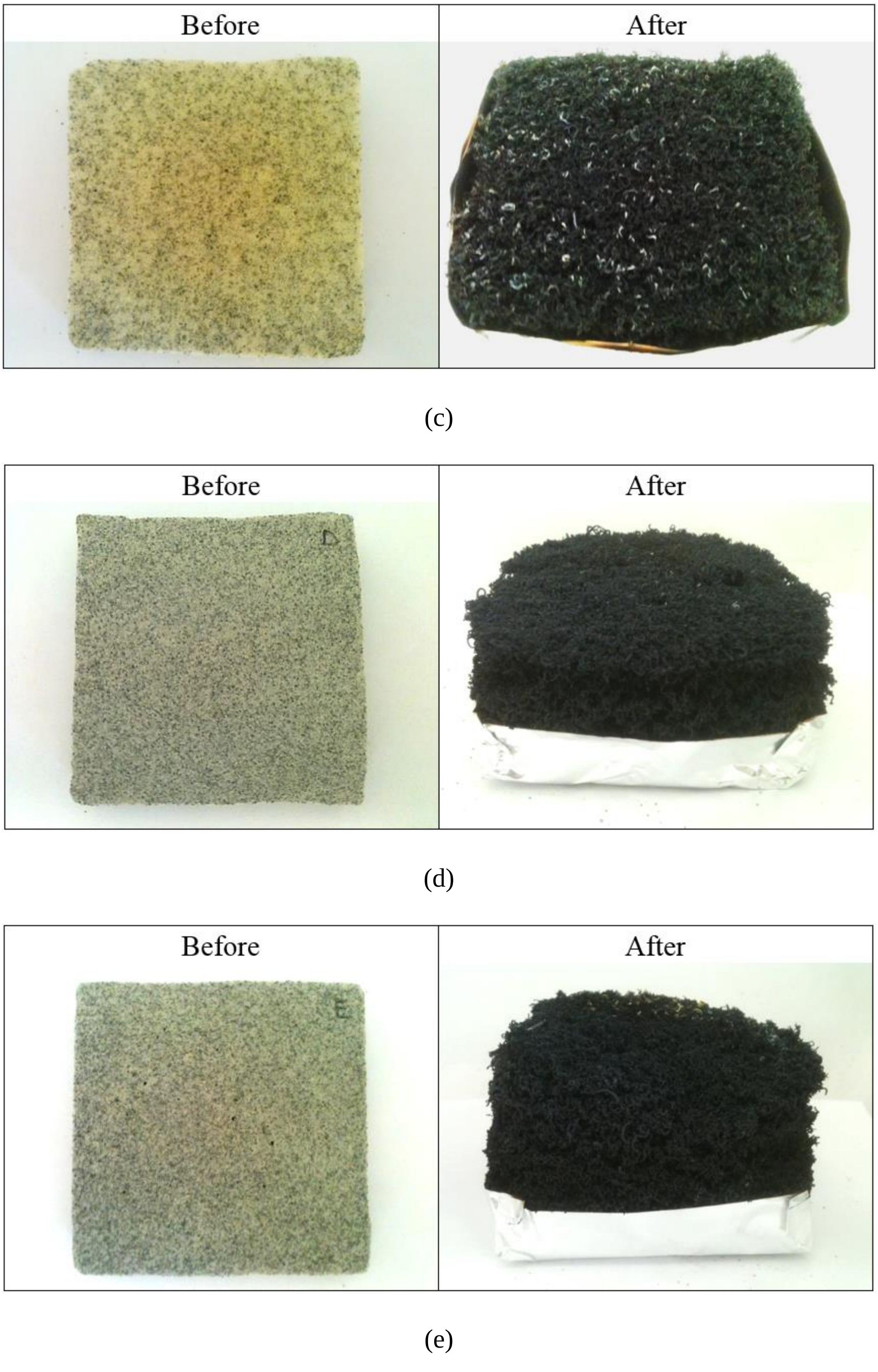
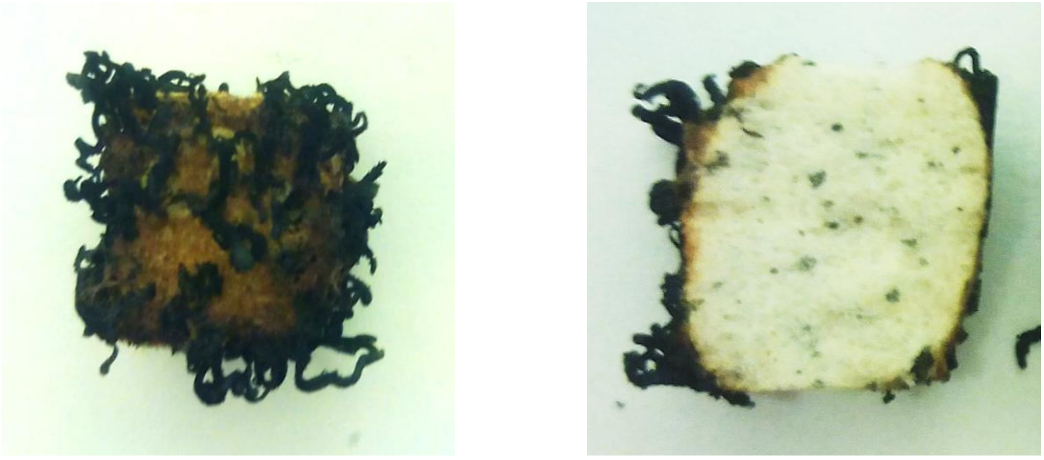


Figure 5. 8 - Images of PUF-EG0 (a), PUF-EG5 (b), PUF-EG10 (c), PUF-EG15 (d) and PUF-EG20 (e) before and after the cone calorimetric tests

In Figure 5. 8 is showed images of the foams before and after the calorimetric analysis and it can be seen the “worm” like structure of EG. Also it can be seen that with the increase of the EG content, the residual mass of samples significantly increase.

In addition of Figure 5. 8, in Figure 5. 9 is showed a photograph of the burned PUF-EG5 and it can be seen that the presence of EG prevents the combustion of the material. Despite that the exterior of the foam is burned, the interior of the foam is intact.



(a) (b)

Figure 5. 9 - Photograph of the top (a) and middle (b) burned PUF-EG5

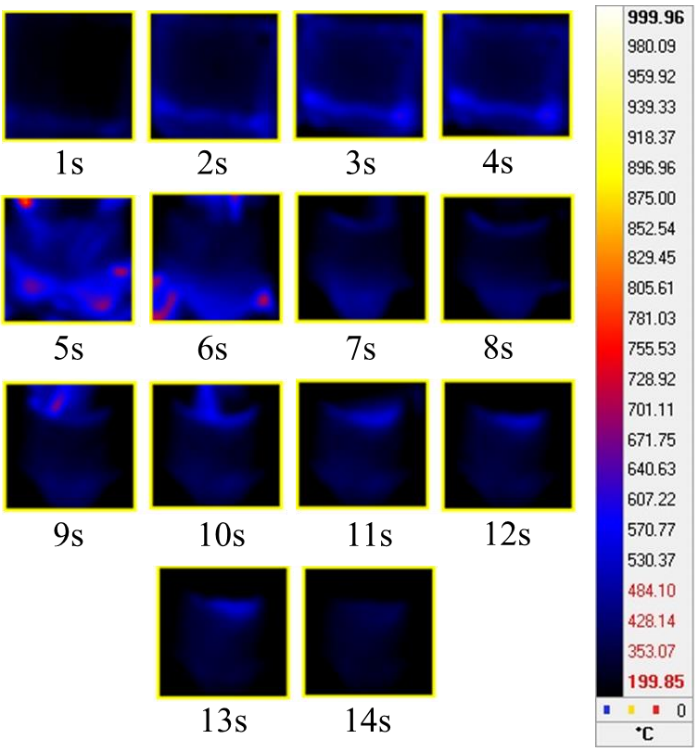
5.4.9. Thermographic analysis of combustion

The combustion of all samples was monitored using Infrared thermography as a function of time. Samples used were cut as cubes with 1 cm edge approximately. The samples were ignited from the bottom. Representative snapshots of the combustion of samples PUF-EG0 (a) and PUF-EG5 (b) are presented in Figure 5. 10. The color palette in the vertical scale spans the temperature range from 200 up to 1000ºC.

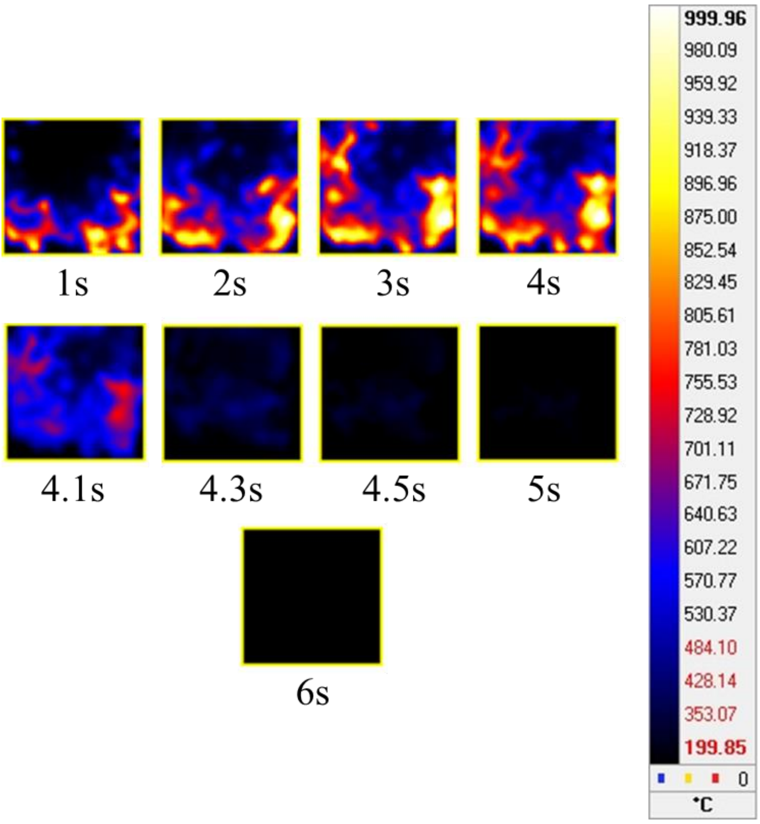
The combustion of sample PUF-EG0 proceeds in a steady way, from bottom to top, and the temperature of the burning front (regions above 500ºC) is typically in the range

600ºC, with rare regions attaining maximum temperature of about 750ºC. The temperature of the sample decreases steadily over more than 10 s, which is the time of the complete combustion of the PU.

The combustion of the composite samples (in the Figure represented by sample PUF-EG5 (b)) proceeds in a much more inhomogeneous way. A maximum temperature of about 1000ºC is quickly attained and concentrated in the ‘‘worm’’ like structure that is developed at the surface of the sample (described before). Then the combustion is seen to stop very suddenly at about 4.0 s. Within about 0.5 s no points observed exceed 450ºC. The behavior of the other filled samples is similar, forming the worm like structure, burning at about the same temperature (1000ºC) and stopping suddenly after a few seconds.



(a)



(b)

Figure 5. 10 - Thermographic images during the combustion of PUF-EG0 (a) and PUF-EG5 (b)

Figure 5. 11 presents the time variation of the maximum temperature points of all the samples during combustion. The higher temperature and time-limited combustion of the composite PUFs is clearly demonstrated. The sharp stop of combustion is also similar, the maximum temperature dropping from about 1000 to near 400ºC within 0.5s for all EG fillerd samples, in clear contrast with the slow decay observed in the neat PUF. These results suggest that EG can also be seen as a flame extinguisher.

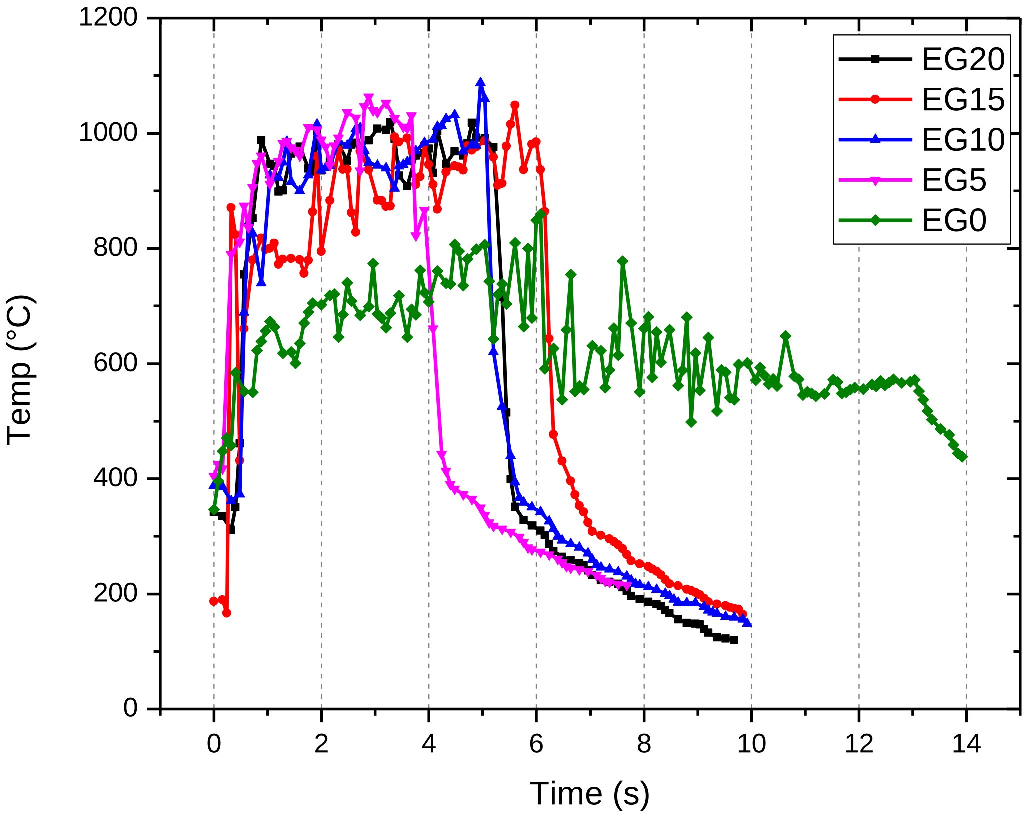


Figure 5. 11 - Time dependence of the maximum temperature of all the samples during combustion.

5.5. Conclusions

In the present study, CG was used to produce ecofriendly PUFs and their reaction to fire were improved by the addition of EG. The presence of EG, proved to have a significant effect on the cellular structure and on the properties of the foams. Whilst it can disrupte the foam structure, increase its density and its thermal conductivity and it can also increase its stiffness, acting as mechanical reinforcement. Furthermore, the presence of EG, has an important effect on the reaction to fire of the materials: increased the CO/CO_2 ratio of the smoke released and the residual mass of the foams after burned. Also due to the physical barrier effect of EG, the *HRR*, the *EHC*, the mass loss ratio and the *SEA* decreased. Nevertheless, the presence of 5 wt % of EG, did not present a significant disruption of the cellular structure nor did it affect adversely the properties of PUFs, whilst having a significant effect on the heat and smoke released, and more importantly acted like a flame extinguisher.

6. Preparation of CG derived foams for sound insulation

This chapter was presented as oral communication (N. V. Gama, R. Silva, C. Pascoal Neto, A. Barros-Timmons, A. Ferreira, "Acoustic and sound absorption properties of crude glycerol and coffee grounds derived polyurethane foams"), at the AMWC *conference, in Stocholm, in 2015. Also was published in the journal of Polymer Testing (Nuno Gama, Rui Silva, António P.O. Carvalho, Artur Ferreira, Ana Barros-Timmons, Sound absorption properties of polyurethane foams derived from crude glycerol and liquefied coffee grounds polyol, Polymer Testing, 62, 13-22, (2017)).*

6.1. Abstract

The main objective of this study was to evaluate the sound absorption properties of rigid PUFs produced from CG and/or liquefied coffee grounds derived polyol (POL). The lignocellulosic compounds of POL proved to have a major influence on the structure and mechanical properties of the foams. Indeed, the POL content increased the cell size of the foams and their stiffness, which subsequently influenced the sound absorption coefficients. The POL derived foam has slightly higher sound absorption coefficient values at lower frequencies, while the CG foam has higher sound absorption coefficient values at higher frequencies. In turn, the foam prepared using a 50/50 (wt/wt) mixture of polyols presents slightly higher sound absorption coefficient values in the medium frequencies range due to a balance between the cell structure and the mechanical properties. The results obtained seem to suggest that the mechanisms involved in sound wave absorption depend on the formulation used to prepare the foams. Additionally higher POL contents improved the thermal stability of PUFs as well as their mechanical properties. From this work the suitability of CG and/or POL derived PUFs as sound absorbing materials has been proven.

Keywords: Polyurethane foams; Crude glycerol, Liquefaction of biomass, Coffee grounds derived polyol, Sound absorption;

6.2. Introduction

PUFs, like other polymers, rely on petroleum feedstock's, however biomass, vegetable oils or industrial by-products have been used to replace petroleum based polyols in the synthesis of PUFs with excellent results.[51,53,54,90,97,220] Indeed, the replacement of petroleum feedstock's by renewable resources has been receiving considerable attention for a long time. The use of this type of feedstock to obtain monomers, polymers and composites has been reviewed back in 2008.[57] Several revision works have also been published regarding production of polyols for the PUs industry which included oxypropylation processes [55] or acid liquefaction [86] of several biomass residues, as well as the modification of vegetable oils.[100] Also, CG which is a byproduct of the biodiesel production, has received much attention.[52,54,155] Considerable studies have been conducted to develop both chemical and biological processes to convert CG to value-added products, such as into hydrogen or ethanol, among many others.[136–142] Nevertheless the successful replacement of petrochemicals by CG and/or biomass polyols in the PUFs production has the potential to reduce their cost and environmental impact. The production of PUFs from CG might also contribute to alleviate the current CG glut and to improve the sustainability of the PUFs industry. Despite of the fact that commercialization of renewable resources based chemicals is gathering speed and major companies such as Dow and Solvay are already actively involved [216] the use of CG and/or biomass polyols in the production of PUFs is still attractive as the lower level of purity required for PUFs production keeps the price competitive.

Foams obtained from renewable resources are mainly rigid due to the small chain length of the polyols, high cross linking density associated with high functionality and in some cases the presence of rigid groups such as aromatic rings also contributes to their stiffness. Therefore this type of materials is generally used in thermal insulation and as structural materials.[252] However, despite of their porous structure, their use as sound absorbers has not received much attention when compared to flexible foams. The latter are known to have good sound absorption properties due to the cavities, channels or interstices present in their structure.[167] When sound waves flow through the open pore cells of a flexible foam, the frictional forces between the air flow and cells wall, convert the sound energy into heat energy.[202,204,269] However, this does not fully explain the sound absorption capability of rigid foams which tend to have a combination of closed porous, partially open and even open cells. Yet, there are others mechanisms of sound absorption: whilst open cells act as a porous absorber, a closed cell can act as a membrane absorber and a partial open cell can act as a Helmholtz absorber. In the case of a membrane absorber, the resonant properties of the system (cavity and borders) provide sound absorption.[203] This type of absorber consists of a constrained space limited by a border ("membrane") which will respond to incident sound waves by vibrating, therefore the material bends and a certain amount of frictional loss results in absorption of sound energy.[203] In turn, an Helmholtz absorber (or resonator) consists of an enclosed volume with a small aperture which will respond to incident sound waves by resonating, thus absorbing sound energy at certain frequencies.[203]

As mentioned above, rigid PUFs generally consists of a combination of open, partially open (closed cells with small pinholes) or fully closed cells and a combination of all of them. Therefore, the application of rigid foams as sound absorbing materials requires adequate understanding of the relationship between the mechanical properties, the porous structure and the sound absorption performance.[201,269–271] Ling *et al*. have described a method of production of rigid PUFs which possess high sound absorption properties, but the relationship between their acoustic properties with the stiffness of the foams it is not discussed.[272] Tiuc *et al*. improved the sound absorption properties of rigid PU foam with the incorporation of textile wastes [273] however, the homogeneity of the material was difficult to achieve and the influence of their mechanical properties on the cellular structure on the sound absorption coefficient values is not discussed. Furthermore, in these works the role of the fillers seems to be crucial for the sound absorption properties, and not necessarily the PU network. Çelebi *et al*. have used leaf fibers in the preparation of composite rigid and flexible foams. Although this filler had a major impact on the sound absorption properties of flexible foams, it had little effect in the case of rigid PUF.[274] In turn, PUFs from liquefied coffee grounds wastes have been produced and the results suggested potential applications of these materials in areas where damping properties can be an added value.[51]

Considering the potential of PUFs from liquefied coffee grounds wastes mentioned above and the attention that CG has been receiving for application in PUFs production, in this work PUFs derived from CG and/or from liquefied coffee grounds polyol were prepared and the relationship between their structure and mechanical properties with their sound absorption capability is discussed.

6.3. Experimental

6.3.1. Materials

The foams studied were produced from the reaction between CG and/or coffee ground derived polyol, with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. CG sample was kindly supplied by *Bioportdiesel* and present a water content of 1.6 ± 0.01, an *AV* of 23.1 ± 0.2 $mg_{KOH}.g^{-1}$ and an OH_{number} of 399.0 ± 4.7 $mg_{KOH}.g^{-1}$. Spent coffee grounds, were kindly provided by *NESTLÉ S.A* (Portugal) and were liquefied using as a solvent mixture of polyethylene glycol (PEG, 99 % purity and average molecular weight of 400), supplied by *Merck* and glycerol (99.5 % purity), purchased from *Sigma-Aldrich*, and catalyzed with sulfuric acid (H_2SO_4, 95–97 % purity) supplied by *Fluka*. The resulting liquefied polyol had a water content of 2.7±0.01, an *AV* of 6.9±0.1 $mg_{KOH}.g^{-1}$ and an OH_{number} of 359.1 $mg_{KOH}.g^{-1}$. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% and a functionality of 2.7 was kindly supplied by *Dow Chemicals*. Tegostab B8404, a polyether-modified polysiloxane was used as silicone surfactant and was supplied by *Evonik*. Polycat 34, a tertiary amine was used as catalyst and supplied by *Air Products*. As blowing agent, distilled water was used.

6.3.2. Production of coffee grounds derived polyol

The study and optimization of the liquefaction process of coffee grounds was previously carried out in a 300 cm^3 reactor.[97] The knowledge obtained was used to produce coffee grounds derived polyol in a 70 L stainless steel vessel. The liquefaction was carried out with 3.3% (wt/wt) of sulfuric acid at atmospheric pressure, at 160 ºC and 80 minutes. A mixture of PEG/Glycerol (9/1 (wt/wt)) was used as solvent and the liquefaction solvents/coffee grounds powder ratio was 6/1 (wt/wt).

6.3.3. Characterization of polyols

The water content, acid value (AV) and hydroxyl number (OH_{number}) of the polyols were determined according to the procedures described in Chapter 1.

6.3.4. Production of PUFs

The polyol component and the corresponding amounts of catalyst (3 parts per polyol wt/wt), surfactant (4 parts per polyol wt/wt) and blowing agent (6 parts per polyol wt/wt), were placed in a polypropylene cup and homogenized using a mechanical stirrer for *ca.* 10 seconds at 700 rpm. Note that the amounts of water present in the polyols were subtracted to the amounts of blowing agent added. Next, the appropriate amount of isocyanate to obtain a $R_{NCO/OH}$=1.10 (ratio between NCO groups of isocyanate and OH groups) was added and the mixture homogenized again. The $R_{NCO/OH}$ values used in the PUFs production were determined using Eq. (11).

$$R_{NCO/OH} = (m_{ISO} \times \%_{NCO}/M_{NCO})/(m_{polyol} \times (OH_{number} + AV)/M_{KOH} \ + (m_{H_2o} + m_{BA}) \times Eq_{H_2o})$$

Eq. (11)

Where $R_{NCO/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH moles of each polyol and water, m_{iso} is the mass (g) of isocyanate, $\%NCO$ is the quantity of NCO groups in the isocyanate (31.1%) and M_{NCO} is the molecular weight of NCO group. m_{polyol} is the mass (g) of each polyol, OH_{number} and AV are the hydroxyl number and the acid value of each polyol respectively ($mg_{KOH}.g^{-1}$). M_{KOH} is the molecular weight of KOH. m_{H2O} is the mass of water present in each polyol, while m_{BA} is the mass of blowing agent (water) added. Finally, Eq_{H2O} is the equivalent of OH groups present in the water. The values of OH_{number}, AV and water content of the mixtures of polyols, were determined by the contribution of each polyol. The foams were obtained by free expansion in the cup mold at room temperature and the PUFs formulations are summarized in Table 6. 1.

Table 6. 1 - Foam formulations

Sample code [a]	CG	POL (PHP)	Isocyanate (PHP)	Catalyst (PHP)	Surfactant (PHP)	Blowing Agent (PHP)
PUF-CG100-POL0	100	0	209	3	4	4.4
PUF-CG75-POL25	75	25	205	3	4	4.1
PUF-CG50-POL50	50	50	202	3	4	3.9
PUF-CG25-POL75	25	75	198	3	4	3.6
PUF-CG0-POL-100	0	100	194	3	4	3.3

[a] *Sample Code (PUF-CGX-POLY): X - wt% of CG; Y – wt% of POL*

6.3.5. Characterization of PUFs

The FTIR, density, thermal conductivity, SEM analysis, BET analysis, open cells content, mechanical properties, DMA and TGA of the foams were determined according to the procedures described in Chapter 1.

The sound absorption coefficient values were obtained using a Brüel and Kjaer, model 4002 standing wave apparatus at the Laboratory of Acoustics of the College of Engineering of the University of Porto. The sound absorption coefficient values were determined measuring the maximum (*Ln*, *Max.*) and minimum (*Ln*, *Min.*) sound pressure levels in a standing wave tube at different frequencies. The sound absorption coefficient value was calculated as the average value of three cylindrical foam pieces with 30, 40 and 50 mm thick and 100 mm in diameter, over the frequency range of 125–4000 Hz. For the interpretation of the sound absorption efficiency, the noise reduction coefficient (NRC, arithmetic mean of absorption coefficients at 250, 500, 1000, and 2000 Hz) was calculated.[275]

6.4. Results and discussion

PUFs are widely used as thermal insulation and sound absorbers materials and in our previous reports, the suitability of renewable feedstocks (CG as well as polyols from biomass) for the production of thermal insulation foams has been reported.[50–52] However, the acoustic properties of this type of foams have not received much attention. In the present work, the relationship between the structure and mechanical properties of PUFs with their sound absorption coefficient values is discussed.

6.4.1. Monitorization of reaction

FTIR spectrophotometry was used to monitor the formation of the urethane linkage resulting from the reaction between the NCO groups of isocyanate and OH groups of CG and/or of coffee grounds derived polyol, as well as to monitor the extent of this reaction. Figure 6. 1 shows the normalized FTIR spectra of the polyols used and of PUFs.

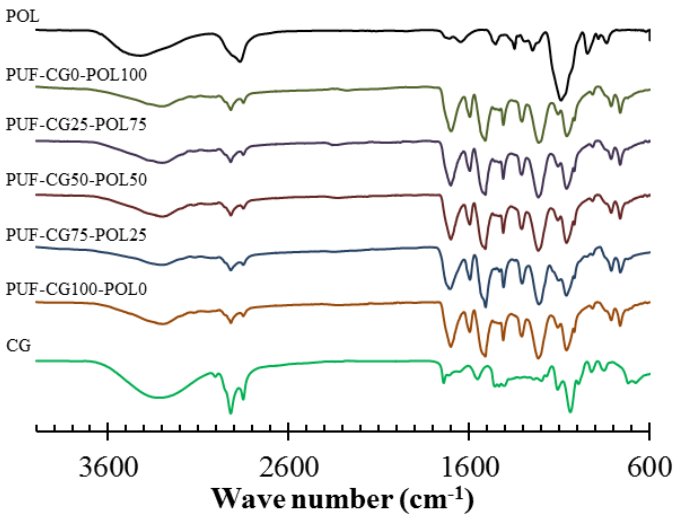


Figure 6. 1 - Normalized FTIR spectra of the polyols used and of PUFs

From Figure 6. 1, it can be seen that the FTIR spectra of polyols presents the band in the 3100–3600 cm^{-1} region which is attributed to the non-bonded stretching vibrations of O-H groups and the bands between 2950 and 2850 cm^{-1} correspond to the asymmetric and symmetric C-H stretching vibrations. The peaks associated with the stretching vibrations of C-O at 1100 and 1240 cm^{-1} are fairly noticed in the POL sample because which are typical of liquefaction solvent (PEG#400) and the peak at 1450 attributed to C-C aromatic groups of the lignocellulosic materials. In turn, in the spectrum of CG, the peaks at 1748 and 1550 cm^{-1} associated with the stretching vibrations of C=O groups, though barely noticed, indicate the presence of esters and salts of carboxyl acids respectively. As regards the PUFs, all normalized FTIR spectra present very similar profiles despite of the differences in isocyanate and polyol content used in the formulations (Table 6. 1). The band in the 3200–3450 cm^{-1} region is attributed to the symmetric and asymmetric stretching vibrations of the N-H of the urethane and of urea groups (resulting from the reaction between water and some of the isocyanate groups). The peak at 1710 cm^{-1} is due to the stretching vibrations of the C=O whilst the nearly overlapped bands between 1540 and 1517 cm^{-1} are attributed to the stretching and bending vibrations of the C-N and N-H of the urethane moieties, respectively.

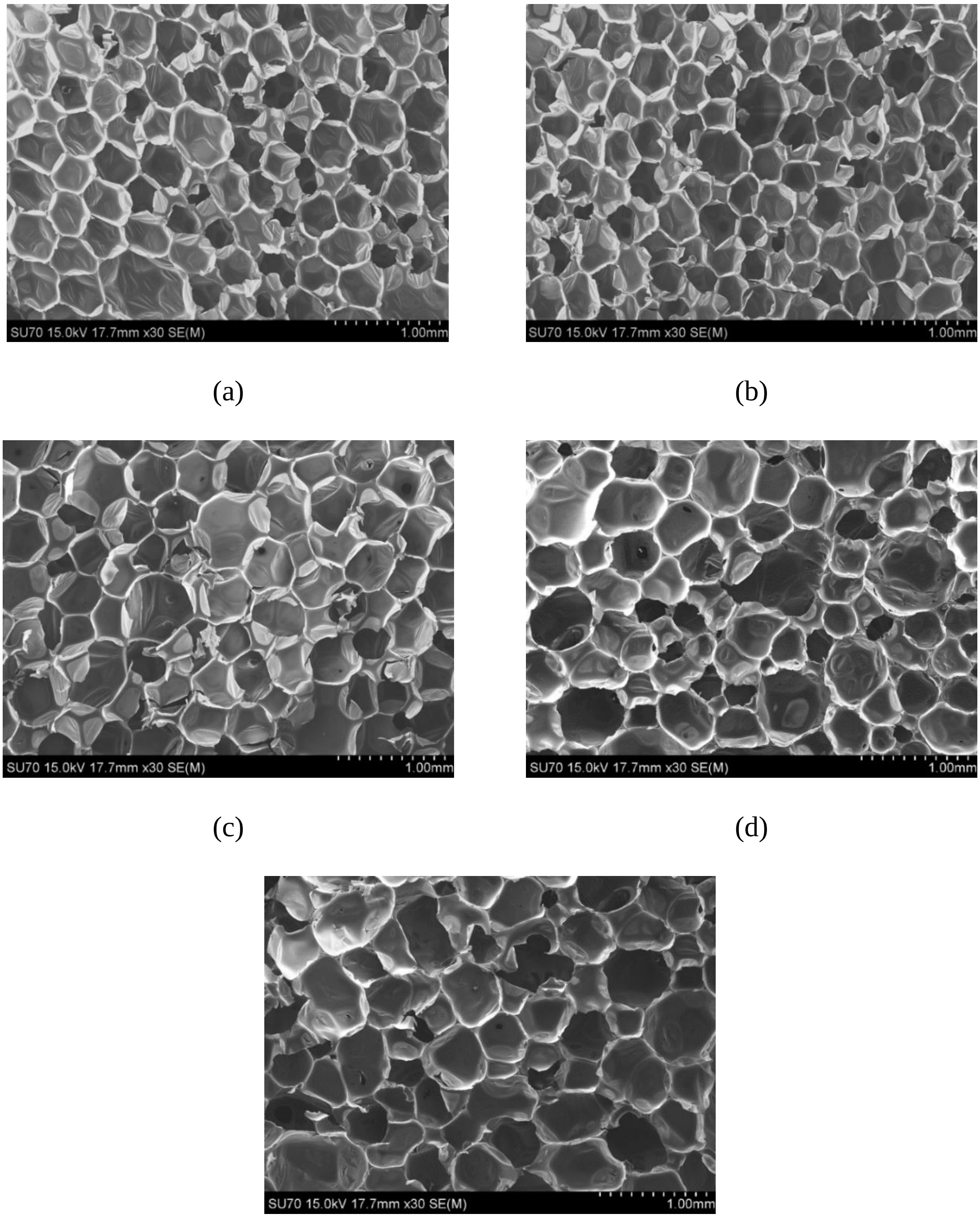
The physical properties of the resulting foams are listed in Table 6. 2.

Table 6. 2 - Properties of PUFs

PUF	Thermal conductivity (W.mK^{-1})	Density (kg.m^{-3})	Average cell size (μm)	Young's modulus (kPa)	Toughness (J.m^{-3})	Compressive stress 10% (kPa)	Tg (°C)
PUF-CG100-P0	0.034 ± 0.001	45.7 ± 2.8	108 ± 18	630 ± 19	15989 ± 1067	46 ± 4	161.6
PUF-CG75-P25	0.035 ± 0.001	43.4 ± 2.7	117 ± 31	974 ± 29	19367 ± 1320	71 ± 4	163.8
PUF-CG50-P50	0.035 ± 0.001	41.2 ± 3.0	154 ± 34	1264 ± 14	22880 ± 1920	84 ± 6	167.1
PUF-CG25-P75	0.036 ± 0.002	39.0 ± 2.6	178 ± 49	1372 ± 23	25520 ± 1161	97 ± 5	170.6
PUF-CG0-P100	0.036 ± 0.002	37.5 ± 2.8	233 ± 65	1535 ± 21	27386 ± 1035	106 ± 4	173.8

6.4.2. Morphology

SEM analysis is an important and versatile tool to inspect foams morphology. During mixing, air bubbles are usually introduced in the reaction mixture and act as nucleation sites for the blowing gas generated from the reaction between isocyanate groups and the blowing agent. The bubbles grow resulting in a closely packed network of bubbles responsible for the typical cellular structure of PUFs.[218] The cell structure of the foams prepared can be observed in Figure 6. 2 where the SEM micrographs of the cross-section surface of PUF-CG100-P0 (a), PUF-CG75-P25 (b), PUF-CG50-P50 (c), PUF-CG25-P75 (d) and PUF-CG0-P100 (e) are presented. The size distribution of the difference foams is illustrated in Figure 6. 3.



(a)

(b)

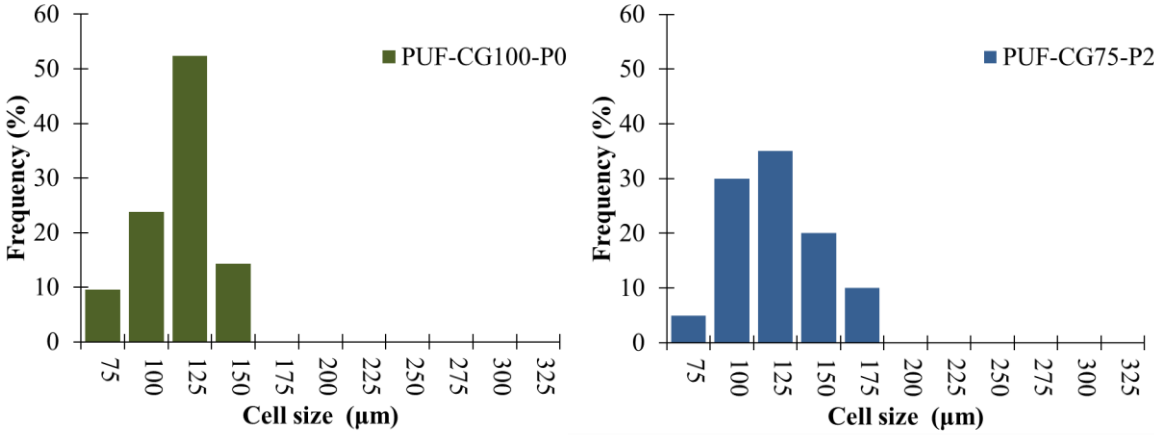
(c)

(d)

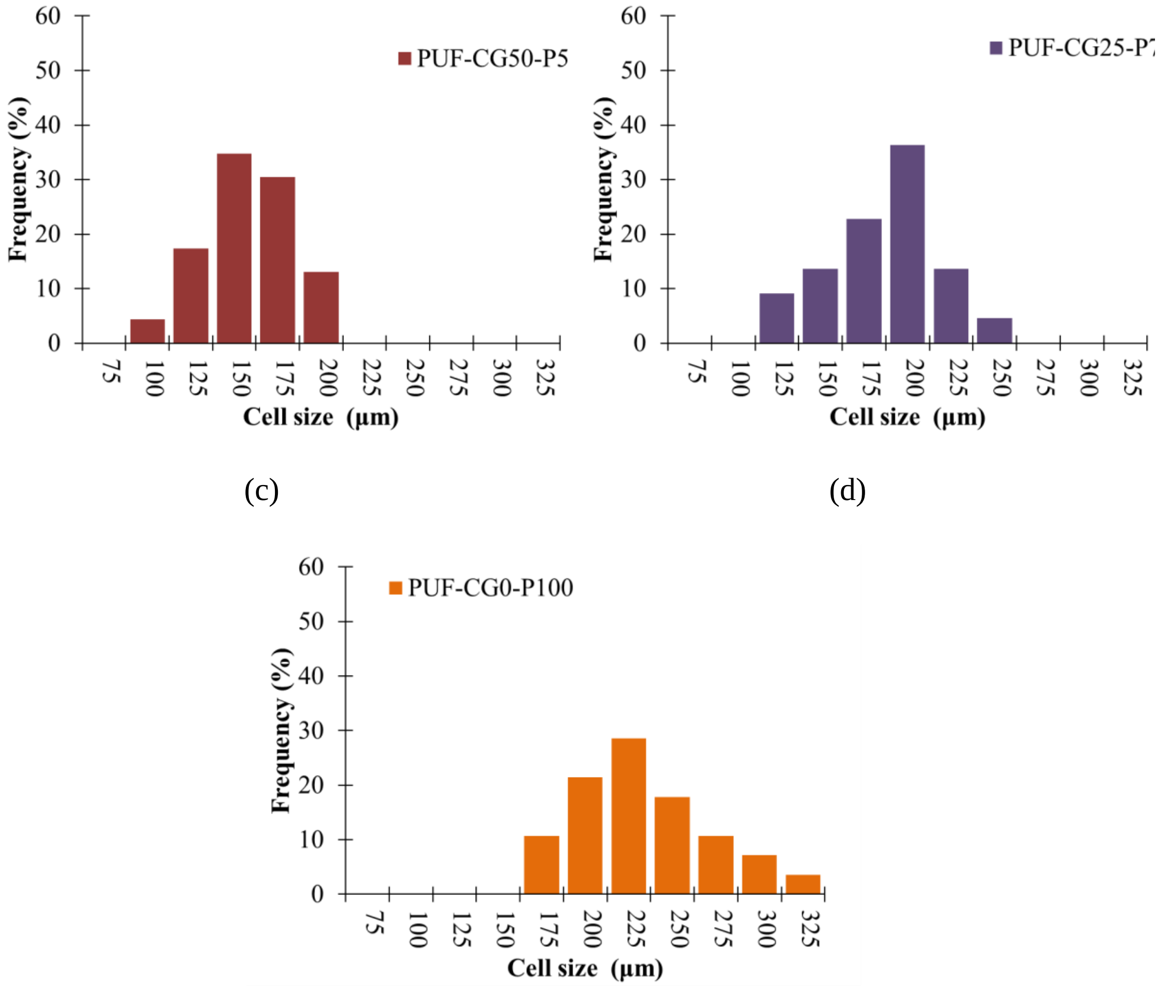
(e)

Figure 6. 2 - Micrographs of the cross-section surface of PUF-CG100-P0 (a), PUF-CG75-P25 (b), PUF-CG50-P50 (c) PUF-CG25-P75 (d) and PUF-CG0-P100 (e)

The typical cellular structure obtained during foam formation is clearly observed in all the samples. It is also noticeable that all foam cells are mainly closed. However, despite of the fact that only 7% (wt/wt) of polyol derived from liquefied coffee grounds polyol was used, some differences are noticed. From Figure 6. 3 it can be seen that the PUF prepared using CG only (PUF-CG100-POL0), presents the smallest average cell size (108 ± 18 µm). In contrast, PUF-CG0-POL100, prepared using only the polyol derived from coffee grounds, presents an average cell size of 233 ± 65 µm. The other PUFs present intermediate values. The differences in size and size distribution can be related to the chemical composition of the polyols used. On the one hand, in the case of CG the presence of free fatty acids which may act as co-surfactants helping the stabilization of the bubbles during foaming may be responsible for the regular size and size distribution obtained.[276] In fact, it is known that the role of the surfactants is to control the process of foaming, producing fewer cells with smaller size as well as regulating the ratio of open/close cells.[51] Moreover, the presence of polyethylene glycol in the POL may retain the blowing gases.



(a) (b)



(c)

(d)

(e)

Figure 6. 3 - Distribution of cell size PUF-CG100-P0 (a), PUF-CG75-P25 (b), PUF-CG50-P50 (c), PUF-CG25-P75 (d) and PUF-CG0-P100 (e)

In turn, PUFs produced using higher amounts of coffee grounds polyol present higher heterogeneity and higher cells size distribution. In fact, the same trend was observed by other authors. Xuejun Pan *et al.* reported that when replacing petroleum based polyol by lignin derived polyols, the shape of the cells of the ensuing foams became less regular and larger cells were formed.[277] Yang Li *et al.* produced kraft lignin-based rigid PUFs and has also observed an increase in cell diameter of foams when higher lignin content was used.[78]

This negative effect on the cellular structure has been attributed to polyols' heterogeneities which affect viscosity and subsequently the foaming process.[277]

Others techniques used to study the textural properties of the foams prepared were the BET analysis and gas pycnometer (open cells content) and the results are listed in Table 6. 3.

Table 6. 3 - Textural properties

PUF	BET Surface Area ($m^2.kg^{-1}$)	Pore volume ($m^3.kg^{-1}$)	% Open cells
PUF-CG100-P0	28300 ± 2100	2.1E-05 ± 2E-06	21.4
PUF-CG75-P25	29700 ± 2400	2.4E-05 ± 4E-06	24.9
PUF-CG50-P50	32400 ± 2800	2.9E-05 ± 2E-06	26.1
PUF-CG25-P75	33900 ± 2900	3.1E-05 ± 3E-06	29.4
PUF-CG0-P100	36900 ± 3000	3.3E-05 ± 2E-06	30.7

The results presented in Table 6. 3 corroborate the previous observations, since it can be seen that the CG derived foam has lower surface area and lower volume. Remarkably, even though differences could barely be distinguish by SEM images, these results clearly show that the increase of open cells content is in line with the higher percentage of coffee grounds derived polyol used in PUFs preparation. These differences in cellular structure have a paramount influence on the sound absorption coefficient values, as it will be discussed further.

6.4.3. Density

Density depends greatly on the cell structure and on the cell size thus, it is an important property of foams because it affects their physical properties. As it can be seen in Table 6. 2, the density of CG derived foam presents a density of 45.7 ± 2.8 kg/m^3 and the addition of coffee grounds derived polyol reduced the density of PUFs down to 37.5 ± 2.8 kg/m^3 for the sample prepared with 100% of this polyol. This is in agreement with the fact that the coffee grounds derived foams present higher average cell sizes and percentage of open cells which result in lower densities.

6.4.4. Mechanical properties

Compressive tests were performed to study the mechanical properties of the PUFs, since they play a major role in the sound absorption capability of foams and can be of interest for potential applications in building construction and car industry. Figure 6. 4 shows the compressive stress-strain plots for PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50, PUF-CG25-P75 and PUF-CG0-P100.

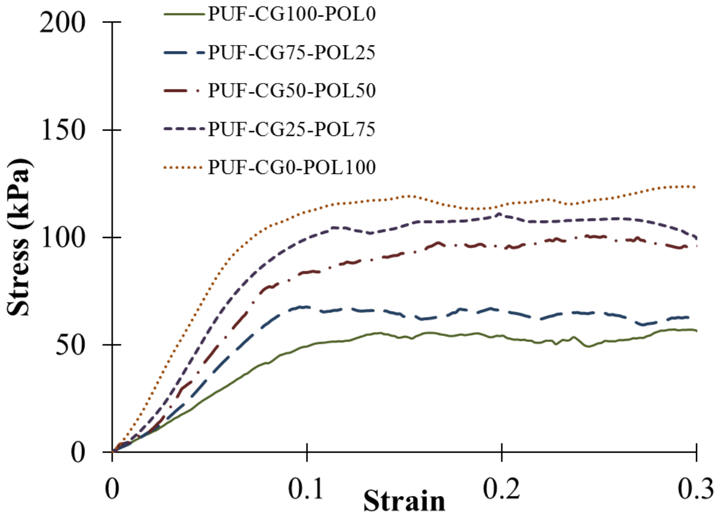


Figure 6. 4 - Compressive stress-strain curves of PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50 PUF-CG25-P75 and PUF-CG0-P100

From Table 6. 2 and Figure 6. 4, it can be seem that the Young’s modulus, compressive strength and toughness increased with the increase of the coffee grounds derived polyol content. Notice should be made that even though the amount of isocyanate used in the formulations decreased as the percentage of coffee grounds derived polyol increased (see Table 6. 1), the mechanical properties were enhanced. This is thought to be attributed to the rigidity of the lignocellulosic compounds and polysaccharides high number of hydroxyl groups, which introduced more crosslinks in the PU network.[78] On the other hand, the mechanical properties of PUF-CG100-P0 may be associated with the presence of low molecular weight fatty acids and methyl esters. These compounds besides acting as co-surfactants during the foaming process, as mentioned before, can also act as plasticizers. As the mechanical properties of the foams are dependent on their density, to exclude the effect of density variations, normalized values of the compressive Young's modulus (specific modulus), toughness (specific toughness) and compressive stress $\sigma 10\%$ (specific stress) were determined and are presented in Table 6. 4.

Table 6. 4 - Young's modulus, compressive stress ($\sigma 10\%$) and toughness normalized for density

Sample code	Specific modulus ($m^2.s^{-2}$)	Specific toughness ($m^2.s^{-2}$)	Specific compressive stress ($m^2.s^{-2}$)
PUF-CG100-P0	13.8	349.9	1.0
PUF-CG75-P25	22.4	446.2	1.6
PUF-CG50-P50	30.7	555.3	2.0
PUF-CG25-P75	35.2	654.4	2.5
PUF-CG0-P100	40.9	730.3	2.8

Considering the data normalized for the density, it is clear that the increase of lignocellulosic compounds content has a direct effect on the mechanical properties of the foams, increasing the stiffness of the foams.

6.4.5. Dynamic mechanical analysis

DMA experiments were carried out in order to obtain further information on the viscoelastic properties of PUFs. Figure 6. 5 displays the temperature dependence of the storage modulus and tan (δ) of PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50, PUF-CG25-P75 and PUF-CG0-P100.

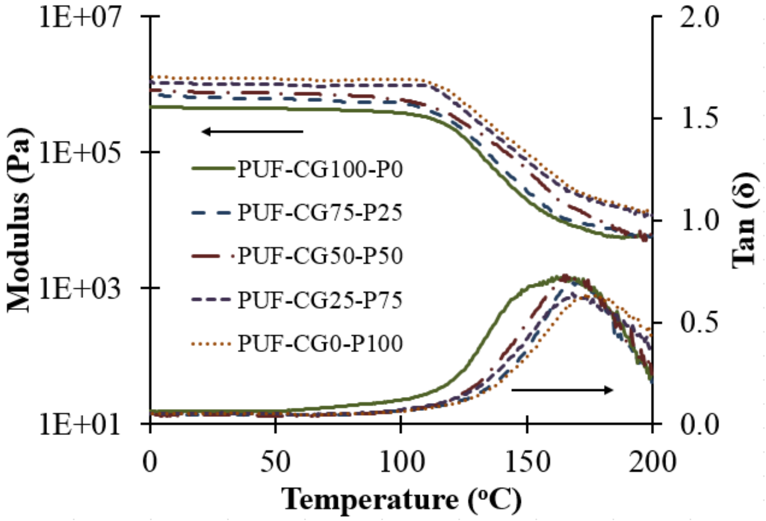


Figure 6. 5 - Temperature dependence of the storage modulus and tan (δ) of PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50 PUF-CG25-P75 and PUF-CG0-P100 at 1 Hz

At room temperature the foams behave as hard solids showing high storage modulus (*E'*) values: 4.8×10^5 and 1.3×10^6 kPa for PUF-CG100-POL0 and PUF-CG0-POL100, respectively with the other PUFs presenting intermediate values. The increase of the modulus of PUFs is related to the increase of the amount of lignocellulosic compounds and polysaccharides, since the content of hard segments increases, as well as higher crosslinking density.[278] In turn, the presence of fatty acids and methyl esters in CG may be associated with the lager area of the tan (δ) peak obtained for PUF-CG100-POL0 indicating better damping properties. As the temperature goes through the glass transition temperature (T_g)

(measured at the top of the tan (δ)), the increase of molecular motion causes the storage modulus to drop abruptly. The introduction of lignocellulosic polyols also increases the *Tg* (161.6 °C and 173.8 °C for PUF-CG100-POL0 and PUF-CG0-POL100, respectively), due to the chemical crosslinks which reduce the mobility of the chains.[278] As for the static mechanical properties, dynamic measurements confirm that the coffee grounds derived polyol increases the stiffness of the foams.

6.4.6. Thermal conductivity

Rigid PUFs are normally used for insulation applications hence, the thermal conductivity (λ) is a property of crucial importance which in turn is related to the foams density and the thermal conductivity of the gas used as blowing agent. Whilst the whole foam only contains a small fraction of PU, since its λ value is much higher than that of the blowing agent, higher density foams have higher thermal conductivity.[238] As it can be seen from Table 6. 2, the thermal conductivity of all foams is very similar. Yet, a clear trend correlating lower thermal conductivity for PUFs prepared using higher amounts of CG can be identified which is in agreement with the SEM results and textural properties.

6.4.7. Thermogravimetric analysis

One important issue of all materials, especially renewable materials, is their thermal stability, hence TGA analysis were carried out under oxygen atmosphere. Figure 6. 6 displays the corresponding TGA curves of PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50, PUF-CG25-P75 and PUF-CG0-P100.

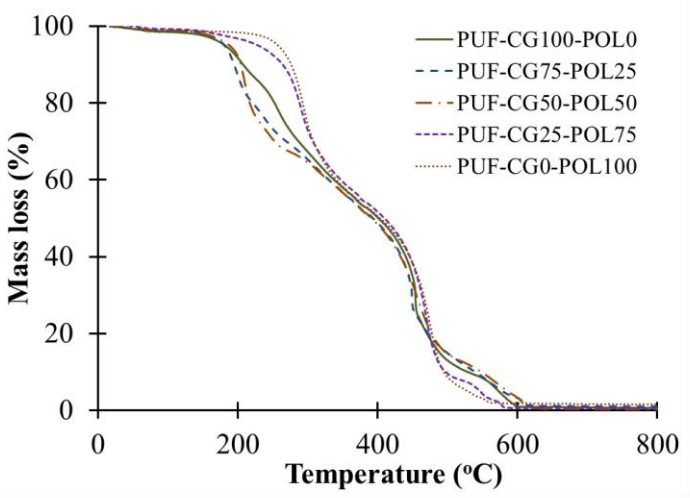


Figure 6. 6 - Thermal degradation of PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50 PUF-CG25-P75 and PUF-CG0-P100

The thermal degradation of PUFs is characterized by the degradation of the hard segments followed by the degradation of the soft segments and at lower temperatures the release of some volatile components may also occur.[227,228] As it can be seen from Figure 6. 6, the decomposition of PUFs shows a very small weight loss at around 100 ºC due to the release of residual water, followed by the two main decompositions steps: *(i)* between 200-290 ºC, related to the thermal decomposition of the hard segments (e.g. urethane groups) and *(ii)* a second, around 450 ºC related to the thermal decomposition of the soft segments.[159] From Figure 6. 6 it is noticeable that the PUF derived from CG starts to thermally degrade at 200 ºC while the PUF derived from coffee grounds derived polyol starts to degrade at 290 ºC. This behavior is attributed to the increase of the lignocellulosic content, since lignocellulosic compounds and polysaccharides act as hard segments.[278] As regards the behavior of foams containing intermediate contents of CG and POL, namely in the first degradation step, this is attributed to the smaller percentage of isocyanate used in their formulations in order to keep the isocyanate index ($R_{NCO/OH}$) constant. These results prove that these materials are thermally stable well beyond ambient temperature.

6.4.8. Acoustic properties

When sound waves hit a surface they can be reflected, transmitted or absorbed/dissipated.[201] Sound wave dissipation can occur in the form of heat energy resulting from the friction between air flowing in and/or out of the cells, as well as in the form of kinetic energy associated with the stretching, bending or buckling of the cells due to the sound pressure.[202] The efficiency of sound absorbers can be assessed by the sound absorption coefficient. The sound absorption coefficient values of the PUFs prepared at frequencies ranging from 125 to 4000 Hz are plotted in Figure 6. 7. Care should be taken that the lines are only a guide to the eye as measurements were taken at specific frequency values.

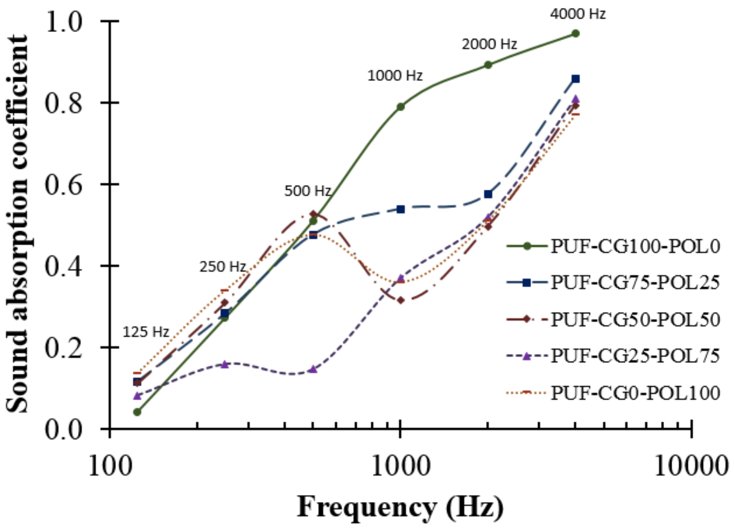


Figure 6. 7 - Sound absorption coefficient values of PUF-CG100-P0, PUF-CG75-P25, PUF-CG50-P50 PUF-CG25-P75 and PUF-CG0-P100 measured in a standing wave apparatus (normal incidence)

From the results presented in Figure 6. 7, it can be seen that the sound absorption coefficient values globally increases with the frequency for all the PUFs. PUF-CG100-

POL0, has higher sound absorption coefficient values which is nearly 1.0 at 4000 Hz. This is due to its better ability to damp the sound wave energy as a result of the smaller percentage of open cells and more regular pore size and structure. This type of cellular structure is associated with increased airflow resistivity which improves sound absorption in the whole range of frequencies.[275,279,280] As mentioned before, the textural properties of this foam may be associated with the presence of fatty acids and methyl esters in CG which act as co-surfactants. Moreover, the role of these compounds as plasticizers may also confer better damping properties.[202]

In turn, the coffee grounds derived foam presents slightly higher sound absorption coefficient values at low frequencies (125–250 Hz). In this range the larger average cell size and higher open cell content may be responsible for its slightly higher sound absorption coefficient values.[204] Yet, as the frequency increases the sound absorption efficiency of this sample is not as good as that of the foam prepared using CG only. This is mainly due to the higher percentage of open cells, irregularity of the cellular structure, as well as the rigidity of the polymer matrix conferred by the lignocellulosic moieties, and the extent of crosslinking. On the one hand the higher porosity and lower density offers less resistance to sound waves as the path is reduced hence, dissipation of sound energy is reduced. Additionally, the rigidity of the polymer matrix prevents vibration of the cell walls and struts, thus energy dissipation is not very efficient at least until high enough frequencies are applied. In other words the conversion of sound energy into kinetic energy, is more difficult due to the lower capability of the cells structure to stretch, band and buckle.[281] All together, these characteristics seem to limit the damping capacity of this foam. However, at frequencies of 4000 Hz the sound absorption coefficient value also reach an interesting value (0.8) indicating that when the energy associated with the sound wave is high enough, the chain segments between crosslinking points gain mobility and are able to absorb the sound energy.

In fact, the rigidity associated with the lignocellulosic moieties cannot be the sole reason for the viscoelastic properties of POL derived foams as it is known that this type of polyol can afford foams with good damping properties using distinct formulations.[51] Nevertheless, in the present study, the combined effect of the rigid lignocellulosic compounds content and crosslinking extent is so significant that addition of 25 wt% of POL already reduced the damping ability of PUF-CG75-POL25.

Interestingly, at medium frequencies (250 and 500 Hz), the highest value of sound absorption (0.53) was achieved by the foam prepared using a 50/50 mixture of CG and coffee grounds polyol. This suggests a balance between the cell structure and mechanical properties of the PUF-CG50-POL50 in this frequency range. However, the performance of the PUF-CG25-POL75 cannot be explained at medium frequency, but it can be speculated that it may derive from limited miscibility CG and POL, and subsequent effect on the pore structure.

In general, for low frequencies, the pore size, structure and density of foams prepared seem to play a major role. In turn, at higher frequencies, the viscoelastic properties of the polymer network seem to be determinant unless high enough energy is involved to overcome the energy barrier associated with the mobility of stiffer moieties. Indeed, as the POL content increased, the stiffness of the ensuing foams increased compromising their ability to damp the sound wave energy up to 2000 Hz. Giwook Sung *et al.* have studied the effect of isocyanate content on the sound absorption coefficient of PUFs and concluded that in high frequency region, the sound absorption coefficient generally decreased with increasing the polymeric MDI content due to the decreased damping effect.[279] Similarly, the use of higher molar mass isocyanates and rigid isocyanates also led to a reduction of the sound absorption efficiency as a result of increased stiffness of the PU matrix at higher frequencies.[275,279,280,282] Curiously, in another study, addition of nanofillers to flexible PUFs yielded higher absorption coefficients even at higher frequencies. This was attributed to the increase of the number of partially opened pores and the enhancing motion of the nanofillers.[280]

In order to assess the potential use of our foams in sound insulation with other foams reported in the literature, the noise reduction coefficients (NRC) were calculate and the values obtained are presented in Figure 6. 8.

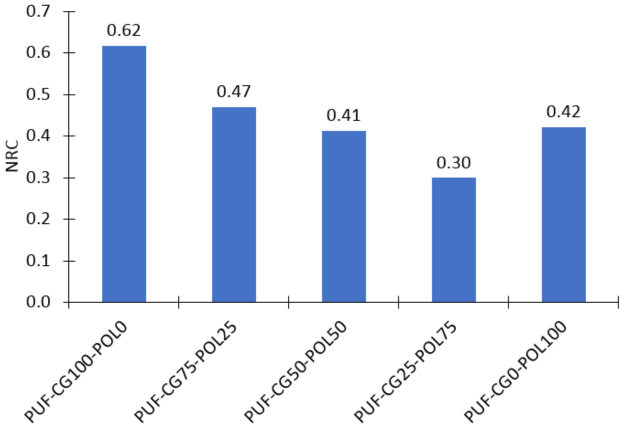


Figure 6. 8 - Noise reduction coefficient (NRC) of samples obtained at frequencies 250 Hz, 500 Hz, 1000 Hz, and 2000 Hz

As it can be conclude from Figure 6. 8 the NRC values of the foams prepared using polyols derived from renewable resources are generally similar to those reported for other materials used as sound absorbers (0.3-0.5) [201,283–285] and in some cases higher, indicating that these rigid foams have potential as sound absorptive materials. Furthermore, judicious blending of these polyols and formulations allows broadening the range of frequencies where rigid PUFs can be efficiently used as sound absorbers.

6.5. Conclusions

In the present study, CG and a liquefied coffee ground derived polyol were used to produce ecofriendly thermally stable sound absorbers PUFs. The properties of the foams indicated that the presence of lignocellulosic material on the coffee ground derived polyol increased the cell sizes and open cells content which increased the sound absorption coefficient values of the foams at low frequencies. On the other hand, the lower stiffness of the CG foams improved the sound absorption coefficient values of the foams at higher frequencies. In the middle frequencies range, the combination of the porous structure and mechanical properties of the foams prepared using a 50/50 mixture of polyols, present higher capability of sound absorption. From this work the suitability of CG and/or POL derived PUFs as sound absorbing materials has been proven even though formulation adjustments are still required in order to promote the formation of a more open and interconnected pore structure in order to increase the sound absorbing properties of foams richer in POL. Finally, from thermal conductivity and TGA measurements, it was observed that these foams are good thermal insulation materials and present thermal stability well beyond ambient temperatures.

7. Production of PURFs from recovered PUs waste materials

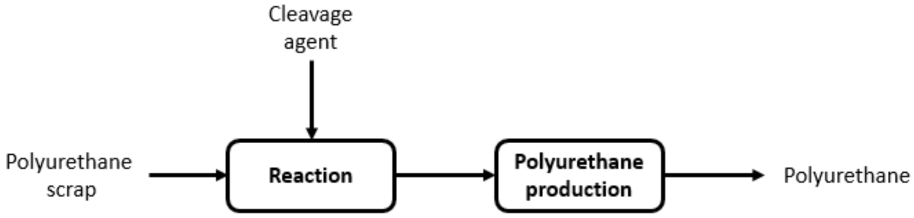
This chapter was submitted for patent application

7.1. Abstract

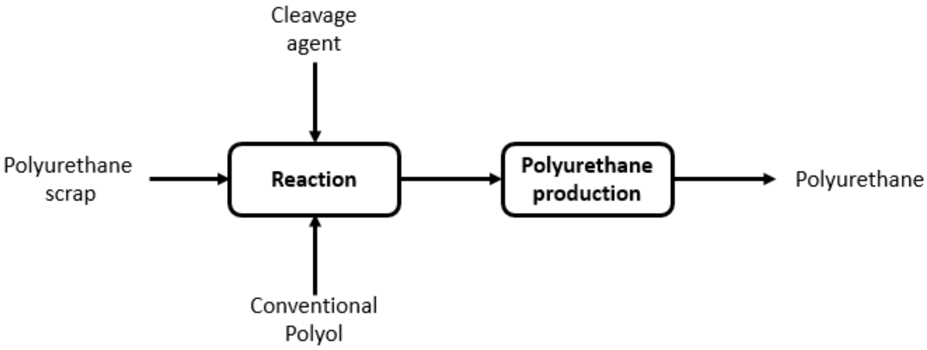
The present subject-matter relates to methods for the recycling of PU scraps using a cleavage agent, without a solvent (Method A), using a conventional polyol as solvent (Method B) or using an inert solvent (Method C). The innovation described herein converts PU scraps into a viscous liquid which can be used as partial or total substitution of the conventional polyols in the production of PU. The final product of the present invention has a wide range of applications including, but not limited to, the production of PU in a form of elastomers, adhesives, paints or foams.

7.2. Technical Field

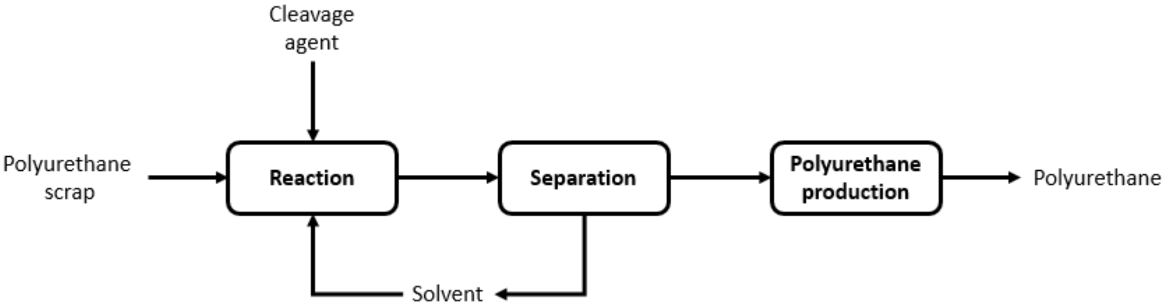
The present disclosure relates to methods for recycling PU scraps using a cleavage agent, without a solvent (Figure 7. 1 (a)), using a conventional polyol as solvent (Figure 7. 1 (b)) or using an inert solvent (Figure 7. 1 (c)). The innovation described herein converts PU scraps into a viscous liquid which can be used as partial or total substitution of the conventional polyols in the production of PUs. The final product of the present invention has a wide range of applications including, but not limited to, the production of PU elastomers, adhesives, paints or foams.



(a)



(b)



(c)

Figure 7. 1 - Recycling methods: method A (a), method B (b) and method C (c)

7.3. Background

PUs are one of the most versatile polymers because it can be used in many applications and forms, such as elastomers, adhesives, paints or foams. They are typically produced from the reaction between the OH groups of a polyol and the NCO groups of an isocyanate. [5] Despite this being the main reaction of production of PUs, other reactions may occur, such as: (i) the reaction of the isocyanate with water, which produces urea and carbon dioxide; (ii) the reaction of the isocyanate with amines, which produces urea; (iii) the reaction of the isocyanate with urethane, which produces allophanate; (iv) the reaction of the isocyanate with urea, which produces biuret; (v) the reaction of the isocyanate with carboxylic acid, which produces amide and carbon dioxide; among others.

The major worldwide consumption of PUs is in the form of a foam which include flexible, semi-rigid or rigid, among others.[3] Due to their variety of applications, the production of PUs has increased in the past decades, leading to an increase of wastes, as well as an increase of the concern about its disposal.[205]

The disposal technology for PUs wastes is major consisted in three types, landfill, incineration and recycling.[207] Due to ecological and environmental problems, landfill and incineration are not valid options. In that sense, PU wastes must be effectively recycled, which is not only a requirement of preventing pollution and environment protection, but is also a need for its production cost reduction and for the material utilization improvement.

There are two major categories for the recycling of PUs: physical recycling and chemical recycling. In physical recycling the PU scraps undergo a mechanical action and are then reused without chemical treatment. The chemical recycling follows the degradation principle. The PU wastes are gradually depolymerized into oligomer and smaller molecules. Functional groups such as carbamic acid ester base, ester, ether bond, among others (present in the ureas, allophanates, biurets, amides, among others) are gradually depolymerized into polyols and/or other oligomers and even smaller molecules depending on the reaction time, reaction temperature and reactants.[207]

Years of research and development lead to many thermo-chemical methods for the recycling of PUs, such as hydrolysis, glycolysis, alcoholysis, aminolysis, among others.[208] All these methods have advantages and drawbacks, but glycolysis is the most commonly used at the industrial scale.

Hydrolysis of PUs is based on the use of overheated steam, which hydrolyzes urethane bonds under the formation of polyols and amines. [209] After separation and purification they can be reused as raw materials for PUs production. However, the separation and purification of hydrolytic products of PUs are insofar costly, making the process economically unattractive.

Aminolysis of PUs is based on breaking urethane bonds with amines (e.g. with dibutylamine or ethanolamine) giving rise to polyols and disubstituted ureas. The final products are oligomeric ureas and amines.[210]

Regarding alcoholysis, the formal substitution of one hydrogen atom in water by an aliphatic group leads to alcohols which may as well be used as cleavage reactants. The reaction is performed in a similar way as the hydrolysis. It requires high temperature under pressure. It was developed hoping for an easier separation of the amines from the polyol methanol mixture, but it the separation is nearly as difficult as with the hydrolysis products and, additionally, methanol has to be evaporated. Numerous patents with respect to alcoholysis are available but none of the process described entered into larger scale application.[211]

The most suitable method currently used in industry is the chemical decomposition of PU network to a polyol mixture, by glycolysis which uses higher boiling glycols as decomposition reagents.[212] A common drawback of PU glycolysis processes is the high energy demands and long reaction time, which significantly restricts their utilization in industry. [213]

All these methods have advantages and drawbacks, with glycolysis being the most commonly used at the industrial scale.

These facts illustrate the technical problem addressed by the present disclosure.

In this invention PU scrap in flakes or in a compressed form are converted into a viscous liquid, using dicarboxylic acids as cleavage agents and using or not a solvent. The final product obtained by the innovation herein described, can be used as partial or total substitution of the conventional polyols in the production of PUs.

7.4. General description

In the present disclosure PU scrap in flakes or in a compressed form are converted into a viscous liquid, using dicarboxylic acids as cleavage agents and using or not a solvent. The final product obtained by the innovation herein described, can be used as partial or total substitution of the conventional polyols in the production of PUs.

From this invention, PU scraps obtained from, but not limited to, flexible foams, semi-rigid foams, rigid foams, elastomers, coatings, adhesives or sealants, among others, can be recycled and reused in the PU production.

In an embodiment of the present disclosure, the cleavage agent is selected from a group comprising, but not limited to, dicarboxylic acids. The dicarboxylic acids are used singly or as a mixture of at least two.

In yet another embodiment, conventional polyols may be selected from a group comprising, but not limited to, ester or ether polyols.

In yet another embodiment, an inert solvent may be selected from a group comprising, but not limited to, paraffin, paraffinic oils and other thermostable and unreactive oils.

In yet another embodiment, the PU flakes can be compressed, but not limited to, pressures from 10 up to 150 bar and temperatures between 120 and 170 ºC, during 2 up to 15 minutes.

In another embodiment, other additives can be additionally used, such as catalysts, UV stabilizers, surfactants, plasticizers, emulsifiers, among others, to adjust/optimize the characteristics required for the final viscous liquid. These additives, although not required, can be used singly or as a mixture of at least two.

In yet another embodiment, the reaction temperature used is, but not limited to, between 150 ºC and 250 ºC.

In another embodiment, the reaction time used is, but not limited to, between 30 minutes and 12 hours.

The present application also refers to a viscous liquid with a viscosity between, but not limited to, 2500 and 10000 cP, an acid value between 0.5 and 2.0 mg_{KOH}/g and an hydroxyl number between 20 and 50 mg_{KOH}/g, which can be used in the production of PUs.

7.5. Detailed description

The present subject-matter discloses a method for the recycling PU scraps using a cleavage agent.

The term “cleavage agent” as used in this application, refers to dicarboxylic acids which break and subsequently link to the carbamate groups of PU.

The term “conventional polyol” as used in this application, refers, but not limited, to conventional ester and/or ether polyols used in the PU production.

The term “inert solvent” as used in this application, refers to a viscous liquid that does not react with the other acidolysis reactants.

PU is one of the most versatile polymers because it can be used in many applications and forms, such as elastomers, adhesives, paints or foams. Due to its variety of applications, the production of PUs has increased in the past decades,[205] leading to an increase of wastes, as well as an increase of the concern about its disposal. Thus, PU wastes must be effectively recycled, both for environment protection and production cost saving.

To overcome the limitations of the methods previously described, a new route to chemical recycling of PUs emerges. It involves the use a cleavage agent (such as, but not limited to, dicarboxylic acids) and or not, the use of conventional polyols (such as, but not limited to, ether or ester polyols) or inert solvents (such as, but not limited to, paraffin oil/wax). The cleavage agents and PU scraps are mixed by mechanical means well known in the art.

The function of the cleavage agent is to react with the carbamic group of PU, as well as with ureas, allophanates, biurets or amides network, which will gradually depolymerize into a polyol and/or other oligomers and small molecules, as described in Figure 7. 2 and Figure 7. 3 and release water and CO_2, where R_1 and R_3 correspond to the conventional polyols chains, R_2 corresponds to the isocyanate chain and R_4 corresponds to the dicarboxylic acid chain.

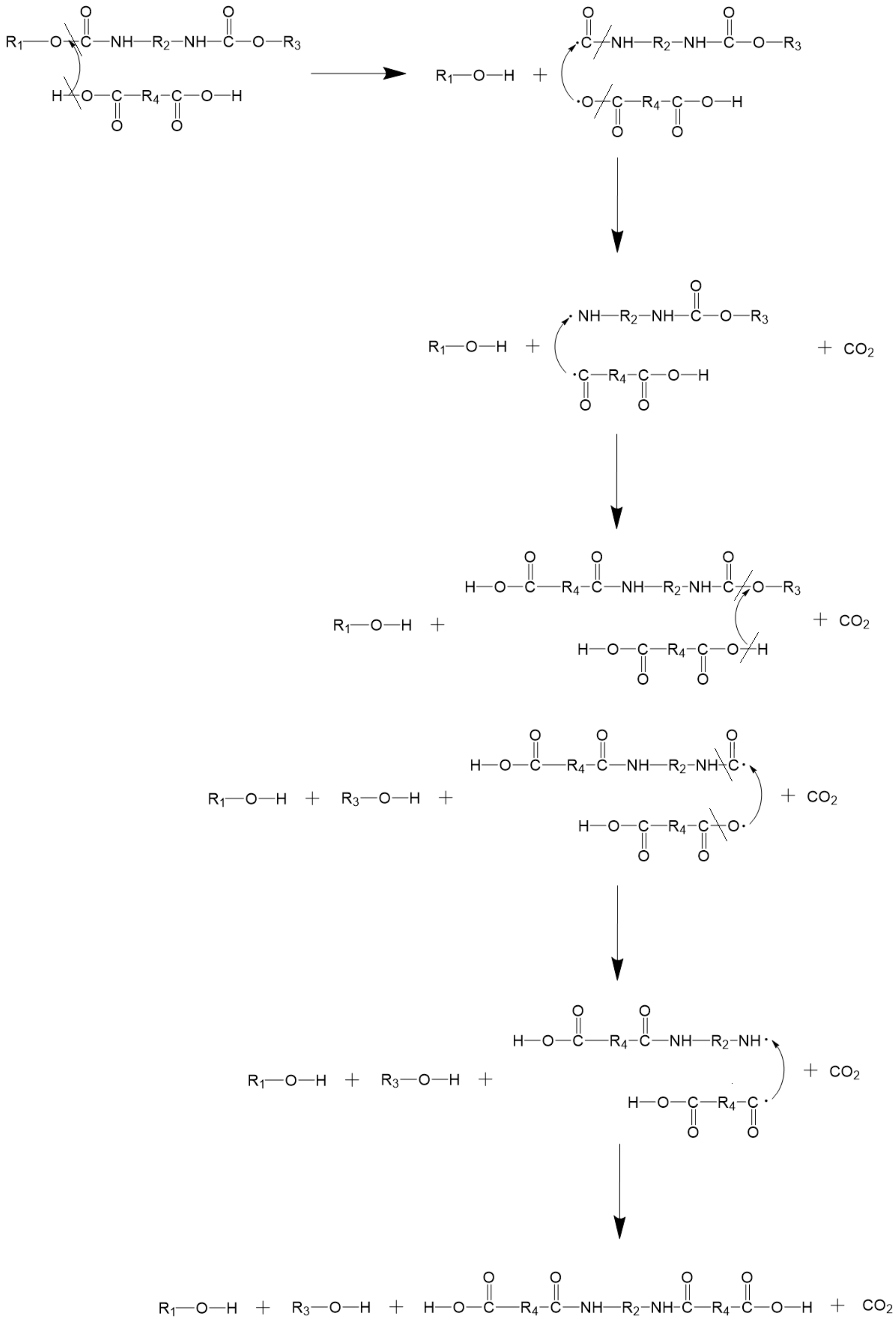


Figure 7. 2 - Mechanism of depolymerisation of PUs

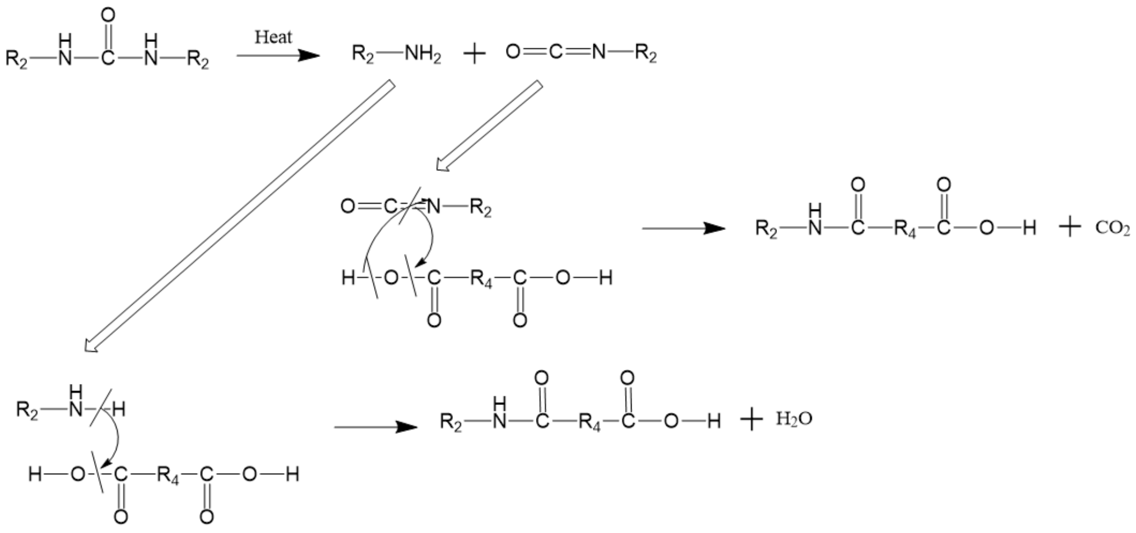


Figure 7. 3 - Mechanism of depolymerisation of amines

The cleavage agents can be, but are not limited to, aliphatic or aromatic diacids. Examples of aliphatic diacids include, but are not limited to, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassilic acid or thapsic acid. Examples of aromatic diacids include cyclohexane carboxylic diacid, and cyclohexane dicarboxylic acids. The dicarboxylic acids can also be used singly or as a mixture of at least two. The carboxyl diacid components used in the process of applicants' invention are well known in the art. The type and quantity of the dicarboxylic acids can be adjusted/optimized with great impact on the characteristics required for the final viscous liquid and type of PU scraps.

Since the main function of the cleavage agent is to react with the carbamic group of the PU, there are no limitations about the type of PUs scraps. This innovation is suitable for the recycling of PUs in the form of elastomers, adhesives, paints or foams, among others. Also, by the invention herein described, there are no limitations on the nature of the polyols that PU is derived from, polyether, polyester, among others; or about PU scraps geometry (shape, size) or color.

The inert solvent used in this innovation can be liquid or solid at room temperature. Conventional polyols (ether or ester polyol) can also be used as solvent. The type and quantity of solvent can be adjusted/optimized to the characteristics required for the final viscous liquid and the type of PU scrap.

Other additives can be additionally used, such as catalysts, UV stabilizers, surfactants, plasticizers, emulsifiers, among others. The type and quantity of these additives can be optimized to adjust the characteristics required for the final viscous liquid and the type of PU scrap.

The temperature of the reaction herein described should be maintained within a specific range to ensure that final product has suitable color, hydroxyl value, molecular weight, acid value, water content, viscosity or molecular weight to be used in the PU production. Low temperature reactions deliver a final product with higher acid value, lower hydroxyl value, higher molecular weight and higher viscosity. Higher temperatures boost kinetics and thus a viscous liquid with lower acid value, higher hydroxyl value, lower molecular weight and lower viscosity, even though a darken color on the final viscous liquid can be observed. The reaction temperature used in this invention is, but not limited to, between 150 ºC and 250 ºC, being suitable between 170 ºC and 210 ºC. Nevertheless, the reaction temperature can be adjusted/optimized to the characteristics required for the final viscous liquid and the type of PU scrap.

In a similar way, reaction time should be maintained within a specific range to ensure that final product has suitable color, hydroxyl value, molecular weight, acid value, water content, viscosity and molecular weight to be used in the PU production. Short time reaction yields a viscous liquid with higher acid value, lower hydroxyl value, higher molecular weight and higher viscosity, while long time reaction delivers a viscous liquid with lower acid value, higher hydroxyl value, lower molecular weight and lower viscosity, and also darkens the final viscous liquid. The reaction time used in this invention is, but not limited to, between 30 minutes and 12 hours, being suitable between 3 and 6 hours. Nevertheless the reaction time can be adjusted/optimized to the characteristics required for the final viscous liquid and the type of PU scrap.

Typically, the method for the recycling of PUs herein described is carried on at atmospheric pressure and uncontrolled composition (air), although other settings can be used, such as vacuum/low pressure or inert atmosphere with nitrogen, among others.

After reaction completion, the viscous liquid must be separated from the inert solvent. Separation processes such as decantation, distillation, evaporation, extraction, fractionation, filtration, sedimentation, gravity separation, among others, can be used, being centrifugation the most industrially viable. After separation, the inert solvent can be reused/refed to the reactor as described in Figure 7. 1.

The viscous liquid obtained can be used as partial or total substitute of the conventional polyols in the production of PUs. The final product of the present invention has a wide range of applications including, but not limited to, the production of PU elastomers, adhesives, paints or foams.

The above described preferred embodiments are intended to illustrate the principles of the invention, but not to limit its scope. Other embodiments and variations of these preferred embodiments can be made without departing from the spirit and scope of the invention as defined in the following claims.

Where ranges are given, endpoints are included. Furthermore, it is to be understood that unless otherwise indicated or otherwise evident from the context and/or the understanding of one of ordinary skill in the art, values that are expressed as ranges can assume any specific value within the stated ranges in different embodiments of the invention, to the tenth of the unit of the lower limit of the range, unless the context clearly dictates otherwise. It is also to be understood that unless otherwise indicated or otherwise evident from the context and/or the understanding of one of ordinary skill in the art, values expressed as ranges can assume any subrange within the given range, wherein the endpoints of the subrange are expressed to the same degree of accuracy as the tenth of the unit of the lower limit of the range.

In addition, it is to be understood that any particular embodiment of the present invention may be explicitly excluded from any one or more of the claims. Where ranges are given, any value within the range may explicitly be excluded from any one or more of the claims. Any embodiment, element, feature, application, or aspect of the compositions and/or methods of the invention, can be excluded from any one or more claims. For purposes of brevity, all of the embodiments in which one or more elements, features, purposes, or aspects is excluded are not set forth explicitly herein.

The above described embodiments are combinable.

The following claims further set out particular embodiments of the disclosure.

The following references are to be considered herewith incorporated in its entirety:

7.6. Example

The present invention will hereinafter be illustrated in further detail by some examples, which by any means should not limit or confine its scope. Several reaction conditions were tested and optimized, in order to provide a viscous liquid with suitable properties to be used in, but not limited to, the production of PUs.

In the recycling of PU scraps according to this invention, 100 g scraps of CG derived rigid PUFs is mixed with 33 g succinic acid (Sigma-Aldrich), 2 g of antioxidant (Tegostab Ortegol AO 6 AF, Evonik), and 100 g of crude glycerol used as solvent, using an high speed mixer, under air atmosphere and atmosphere pressure. The mixture is heated up to 215 ºC, during 30 min. The resulting viscous liquid have a brown color, an hydroxyl value of 1169.0 mg_{KOH}/g, an acid value of 8.9 mg_{KOH}/g and an water content of 0.29%. This viscous liquid has used as 25% (w/w) of substitution of the crude glycerol in the production of rigid PUFs, and ensuing foams presented a density of 48.0 kg/m^3, a young modulus of 371.2 kPa, a toughness of 7928.6 J/m^3 and compressive stress (10%) of 30.9 kPa, proving the suitability of this recycling method.

7.7. Claims

1. A method for recycling waste of PUs comprising an acidolysis reaction and a dicarboxylic acids used as a cleavage agent wherein the quantity of cleavage agent is, but no limited between 12.5-25 % ($w_{\text{cleavage agent}}/w_{\text{total mass}}$).
2. The method according to claim 1 wherein the thermosetting PUs wastes are derived, but no limited from elastomers, adhesives, paints, foams or mixtures thereof.
3. The method according to any of the previous claims wherein the cleavage agent is, but no limited a dicarboxylic acid.
4. The method according to any of the previous claims wherein the quantity of cleavage agent is, but no limited between 15-25% ($w_{\text{cleavage agent}}/w_{\text{total mass}}$), preferably 16-20% ($w_{\text{cleavage agent}}/w_{\text{total mass}}$).
5. The method according to any of the previous claims wherein the dicarboxylic acids are, but no limited aliphatic diacid, aromatic diacid, or mixtures thereof.
6. The method according to any of the previous claims wherein the succinic acid is used.

7. The method according to claim 6 wherein aromatic dicarboxylic acids are select from a list consisting, but no limited of cyclohexane carboxylic acids and mixtures thereof.
8. The method according to any of the previous claims further comprising the no use of a solvent into the acidolysis reaction.
9. The method according to any of the previous claims further comprising the addition of a solvent into the acidolysis reaction.
10. The method according to any of the previous claims wherein the quantity of the solvent is, but no limited between 35-60% ($w_{\text{inert solvent}}/w_{\text{total mass}}$).
11. The method according to the preceding claim wherein the quantity of the solvent agent is between 40-45% ($w_{\text{inert solvent}}/w_{\text{total mass}}$).
12. The method according to any of the previous claims wherein the solvent is an inert solvent or a conventional polyol.
13. The method according to the previous claim wherein conventional polyols are an ether or an ester polyol, or mixtures thereof.
14. The method according to claim 9 wherein the solvent is, but not limited a paraffin, wax, or a similar chemical.
15. The method according to any of the previous claims further comprising the addition of an additive into the acidolysis reaction.
16. The method according to any of the previous claims wherein the additive is selected from a list consisting of catalysts, UV stabilizers, surfactants, plasticizers, emulsifiers, antioxidants or mixtures thereof.
17. A polyol mixture obtainable by the method of any of the preceding claims.
18. The polyol mixture obtainable according to the method described in any one of the preceding claim comprising a hydroxyl value between, but not limited 20.0 and

50.0 mg_{KOH}/g, an acid value of 0.2 and 5.0 mg_{KOH}/g, an water content of 0.1% and 5.0% and a viscosity of 500 and 10000 Cp.

8. Conclusions

Rigid PUFs are widely used in construction where its superior insulation properties are required. Despite their many advantages, one important drawback of these materials is that they are highly dependent on petroleum based reactants. Nevertheless, considerable efforts have been focus in reducing this dependence by substituting the petroleum based polyols by eco-friendly reactants, such as CG, which is a sub-product of the biodiesel production. However to achieve the fully acceptance of CG by the PUFs manufactures, some problems must be settled, which are the aims of this PhD thesis.

Probably the most important problem of the use of CG in the production of PUFs is that depending on the feedstock used in the biodiesel production as well as the reaction conditions used, the CG composition can present high variability. In that sense to access the influence of the CG composition on the properties of PUFs different CG samples were used to produce foams and to evaluate the effect of CG composition on the properties of resulting PUFs. It was observed that indeed the “impurities” of the CG, such as methyl esters and fatty acids, seem to affect the foaming process, the crosslinking density and can have some surfactant effect. Therefore foams with higher content of fatty acids and methyl esters present lower Young’s modulus, toughness and compressive stress values. In turn, due to the surfactant effect, the resulting foams presented a more homogeneous cellular structure. Other properties, such as the thermal stability and thermal conductivity are not significantly affected by the presence of fatty acids and esters, since all CG derived PUFs were thermally stable up to 180 ºC and exhibited low densities and low thermal conductivities. Additionally the impact of the use of CG towards sustainability of foams production yielded promising results.

Whatever the application of the foams in mind, the optimization of the foams formulation must be achieved. Also very important is to have knowledge about the relationship between the foam formulations and the properties of the ensuing PUFs. In that sense, PUFs were produced using different formulations and the effects of the reactant contents on the properties of the PUFs were statistically evaluated. It was concluded that the density and thermal conductivity of the foams are highly dependent on the blowing agent and surfactant contents, while the mechanical properties are essentially related with the content of isocyanate and catalyst.

Being the thermal insulation, the main property/application of rigid PUFs, to distinguish the CG derived PUFs from others thermal insulation materials, the enhancement of this property gains paramount importance. The addition of PCMs, since they have high capability to store/release heat energy, could be the solution, bringing the possibility of thermal regulation (thermal confort). Additionally, the addition of EG could improve the efficiency of the PCMs. However, despite of the improvement observed of the mechanical properties of the foams filled with PCMs and/or EG, both thermal conductivity and density of the composites increased beyond usefull values, as no improvement in thermal confort were achieved. Hence, adjustments on the PUFs formulation are still required.

One major drawback of PUFs, is that they burn very easily. Since a greater attention has been paid to the fire safety of materials, the fire resistance of the PUFs must be improved. EG, being a well-known flame retardant, is highly used to improve the fire reaction of PUFs. Even though the presence of 5% of EG can disrupt the foam structure, increase its density and its thermal conductivity, it was also observed that it increases the stiffness of the foams, acting as mechanical reinforcement. More important, the presence of EG decrease of the quantities of heat and smoke released when the foams are burned. This results in a reduction on the mass loss ratio and an increase of the residual mass. Furthermore the reults obtained, suggests that EG stops suddenly the combustion, suggesting it acts like a flame extinguisher.

Also to increase the added value of the CG derived PUFs, other properties can be improved, such as their acoustic absorption properties. Usually, PUFs used as sound absorption materials are flexible with high content of open cells. One solution to turn rigid PUFs in an adequate sound absorption material is to partially substitute CG by another eco-friendly polyol, such as a polyol derived from the liquefaction of the coffee grounds. In that sense, CG and a liquefied coffee ground derived polyol were used to produce sound absorbers PUFs. As expected, the presence of this coffee ground derived polyol changed the properties of PUFs, since its presence increased the cell sizes and open cells content which increased the sound absorption coefficient values of the foams at low frequencies. On the other hand, the lower stiffness of the CG foams improved the sound absorption coefficient values of the foams at higher frequencies. In the middle frequencies range, the combination of the porous structure and mechanical properties of the foams prepared using a 50/50 mixture of polyols, present higher capability of sound absorption.

Finally, from the prespective of the circular economy, the PUFs residues must have a suitable destination, instead of being dispose in land field or incinerated. Despite of several chemical or physical recycling methods reported in literature, a new chemical method, the acidolysis is emerging. This involves the convertion of PUFs wastes into a reactant, which can be used in the production of new PUFs. To test the effectiveness of this method, CG derived PUFs wastes were milled and filled to a reactor. Also to the reactor was added succinic acid, an antioxidant and CG. The reaction product obtained was used as 25% (w/w) of substitution of CG in the production of foams. Since the resulting foams presented similar properties, comparing with the original ones, it was demonstrated the suitability of this recycling method.

The main goal of this PhD thesis was to improve the sustainability of the PUFs production. The main route to achieve the sustainability was to produce foams from an eco-friendly polyol: the CG. The CG was used directly, without any pre-treatment or purification step and the ensuing foams presented excellent properties, meaning that CG is a suitable feedstock for the production of PUFs. Furthermore, to increase the added value of these materials, their reaction to fire and their sound absorption properties were enhanced successfully. Finally, a recycling process was developed for these foams which helps to improve even more the sustainability of the PUFs industry.

9. References

[1] S.-T. Lee, N.S. Ramesh, Polymeric Foams: Mechanisms and Materials, CRC Press, London and New York, 2004.

[2] M. Szycher, Szycher's Handbook of Polyurethanes, 2nd ed., CRC Press, 2006.

[3] K. Ashida, Polyurethane and Related Foams Chemistry and Technology, Taylor & Francis Group, Florida, 2007.

[4] P. Król, Linear Polyurethanes: Synthesis Methods, Chemical Structures, Properties and Applications, VSP, 2008.

[5] C. Prisacariu, Polyurethane Elastomers From Morphology to Mechanical Aspects, Springer, 2011.

[6] M. Ionescu, Chemistry and Technology of Polyols for Polyurethanes, Rapra Technology, 2005.

[7] E. Sharmin, F. Zafar, Polyurethane: An Introduction, InTech, London, 2012.

[8] Polyurethane market Size, Share, Price - Industry Report, Glob. Insights Mark. (2016). https://www.gminsights.com/industry-analysis/polyurethane-PU-market (accessed October 31, 2016).

[9] M.F. Sonnenschein, Polyurethanes : science, technology, markets, and trends, Wiley, 2014.

[10] W.D. Vilar, Quimica e tecnologia dos poliuretanos, 2nd ed., Vilar Consultoria, 1998.

[11] S.N. Singh, Blowing Agents for Polyurethane Foams, Rapra Technology, 2002.

[12] T.T. Healy, Applications of Polyurethane Foams in the Motor Industry, in: Proc. Symp. Polyurethane Foam., 1963: pp. 77–91.

[13] S. Bron, A. Sluszny, D. Peled, D. Perle, M. Gelmont, O. Cohen, et al., Scorch prevention in flexible polyurethane foams, US 20080237555 A1, 2006.

[14] W.-Y. Jang, A.M. Kraynik, S. Kyriakides, On the microstructure of open-cell foams and its effect on elastic properties, Int. J. Solids Struct. 45 (2008) 1845–1875.

[15] A. Kausar, Polyurethane Composite Foams in High-Performance Applications: A Review, Polym. Plast. Technol. Eng. (2017) 1–24.

[16] S.G.G. Silva M.C., Takahashi J.A., Chaussy D., Belgacem M.N., Composites of rigid polyurethane foam and cellulose residue, J. Appl. Polym. Sci. 117 (2010) 3665 – 3672.

[17] G.P. Otto, M.P. Moisés, G. Carvalho, A.W. Rinaldi, J.C. Garcia, E. Radovanovic, et al., Mechanical properties of a polyurethane hybrid composite with natural lignocellulosic fibers, Compos. Part B Eng. 110 (2017) 459–465.

[18] I. Ibrahim Marhoon, A. Kais Rasheed, Mechanical and Physical Properties of Glass Wool-Rigid Polyurethane Foam Composites, Coll. Eng. J. 18 (2015) 41–49.

[19] V. Yakushin, L. Bel'kova, I. Sevastyanova, Properties of rigid polyurethane foams filled with glass microspheres, Mech. Compos. Mater. 48 (2012) 579–586.

[20] D.-A. Şerban, O. Weissenborn, S. Geller, L. Marşavina, M. Gude, Evaluation of the mechanical and morphological properties of long fibre reinforced polyurethane rigid foams, Polym. Test. 49 (2016) 121–127.

[21] M. Zieleniewska, M.K. Leszczyński, L. Szczepkowski, A. Bryśkiewicz, M. Krzyżowska, K. Bień, et al., Development and applicational evaluation of the rigid polyurethane foam composites with egg shell waste, Polym. Degrad. Stab. 132 (2016) 78–86.

[22] A. Oushabi, S. Sair, Y. Abboud, O. Tanane, A. El Bouari, An experimental investigation on morphological, mechanical and thermal properties of date palm particles reinforced polyurethane composites as new ecological insulating materials in building, Case Stud. Constr. Mater. 7 (2017) 128–137.

[23] A. Bryśkiewicz, M. Zieleniewska, K. Przyjemska, P. Chojnacki, J. Ryszkowska, Modification of flexible polyurethane foams by the addition of natural origin fillers, Polym. Degrad. Stab. 132 (2016) 32–40.

[24] M. Antunes, Á. Cano, L. Haurie, J.I. Velasco, Esparto wool as reinforcement in hybrid polyurethane composite foams, Ind. Crops Prod. 34 (2011) 1641–1648.

[25] K.M. You, S.S. Park, C.S. Lee, J.M. Kim, G.P. Park, W.N. Kim, Preparation and characterization of conductive carbon nanotube-polyurethane foam composites, J. Mater. Sci. 46 (2011) 6850–6855.

[26] T. He, X. Liao, Y. He, G. Li, Novel electric conductive polylactide/carbon nanotubes foams prepared by supercritical CO2, Prog. Nat. Sci. Mater. Int. 23 (2013) 395–401.

[27] J. Espadas-Escalante, F. Avilés, P. Gonzalez-Chi, A. Oliva, Thermal conductivity and flammability of multiwall carbon nanotube/polyurethane foam composites, J. Cell. Plast. 53 (2017) 215–230.

[28] D.-X. Yan, K. Dai, Z.-D. Xiang, Z.-M. Li, X. Ji, W.-Q. Zhang, Electrical conductivity and major mechanical and thermal properties of carbon nanotube-filled polyurethane foams, J. Appl. Polym. Sci. 120 (2011) 3014–3019.

[29] J.M. Kim, Y. Lee, M.G. Jang, C. Han, W.N. Kim, Electrical conductivity and EMI shielding effectiveness of polyurethane foam-conductive filler composites, J. Appl. Polym. Sci. 134 (2017) 1–9.

[30] R.M. Hodlur, M.K. Rabinal, Graphene based polyurethane material: As highly pressure sensitive composite, in: Phys. Educ. Res. Conf., Philadelphia, 2012: pp. 1279–1280.

[31] M. Strankowski, D. Włodarczyk, Ł. Piszczyk, J. Strankowska, ukasz, J. Strankowska, Thermal and Mechanical Properties of Microporous Polyurethanes Modified with Reduced Graphene Oxide, Int. J. Polym. Sci. 2016 (2016) 1–8.

[32] Z. Liu, D. Shen, J. Yu, W. Dai, C. Li, S. Du, et al., Exceptionally high thermal and electrical conductivity of three-dimensional graphene-foam-based polymer composites, RSC Adv. 6 (2016) 22364–22369.

[33] S. Zhang, Y. Li, L. Peng, Q. Li, S. Chen, K. Hou, Synthesis and characterization of novel waterborne polyurethane nanocomposites with magnetic and electrical properties, Compos. Part A Appl. Sci. Manuf. 55 (2013) 94–101.

[34] C. Yufei, L. Zhichao, T. Junyan, Z. Qingyu, H. Yang, Characteristics and Properties of TiO2/EP-PU Composite, J. Nanomater. 2015 (2015) 1–7.

[35] E. Mussatti, C. Merlini, G.M. de O. Barra, S. Güths, A.P.N. de Oliveira, C. Siligardi, Evaluation of the properties of iron oxide-filled castor oil polyurethane, Mater. Res. 16 (2013) 65–70.

[36] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Springer Netherlands, Dordrecht, 2004.

[37] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, J. Am. Chem. Soc. 73 (1951) 373–380.

[38] ASTM D6226 - 15, Standard Test Method for Open Cell Content of Rigid Cellular Plastics, 2015.

[39] J. Grimminger, K. Muha, Silicone Surfactants for Pentane Blown Rigid Foam, J. Cell. Plast. 31 (1995) 48–72.

[40] BASF, Polyurethanes as insulation material, (2014). http://www.polyurethanes.basf.de/pu/Great_Britain/insulation/insulation (accessed January 03, 2018).

[41] Federation of European Rigid Polyurethane Foam Associations, Thermal insulation materials made of rigid polyurethane foam (PUR/PIR), 2006.

[42] A.D.- 15, Standard Test Method for Compressive Properties of Rigid Plastics, 2015.

[43] C. Defonseka, Practical Guide to Flexible Polyurethane Foams Practical Guide to Flexible Polyurethane Foams, Smithers Rapra, 2013.

[44] ASTM D4662 - 15, Standard Test Methods for Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols, 2015.

[45] ASTM D6304 - 07, Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration (Withdrawn 2016), 2007.

[46] ASTM D4878 - 15, Standard Test Methods for Polyurethane Raw Materials: Determination of Viscosity of Polyols, 2015.

[47] S. Tan, T. Abraham, D. Ference, C.W. Macosko, Rigid polyurethane foams from a soybean oil-based Polyol, Polymer. 52 (2011) 2840–2846.

[48] Green and Bio Polyols Market by 2021, Mark. Mark. (2015). http://www.marketsandmarkets.com/PressReleases/Green-and-Bio-Polyols.asp (accessed July 10, 2017).

[49] Bio-based Polyols Market Report Trends, Analysis, Forecast, Micro Mark. Monit. (2013). http://www.micromarketmonitor.com/market-report/bio-based-polyols-reports-1739790449.html (accessed July 10, 2017).

[50] N. V Gama, B. Soares, C.S.R. Freire, R. Silva, C.P. Neto, A. Barros-Timmons, et al., Rigid polyurethane foams derived from cork liquefied at atmospheric pressure, Polym. Int. 64 (2014) 250–257.

[51] N. V. Gama, B. Soares, C.S.R. Freire, R. Silva, C.P. Neto, A. Barros-Timmons, et al., Bio-based polyurethane foams toward applications beyond thermal insulation, Mater. Des. 76 (2015) 77–85.

[52] A. Ferreira, N.V. Gama, B. Soares, C.S.R. Freire, A. Barros-Timmons, I. Brandão, et al., Method for production of rigid polyurethane foams using unrefined crude glycerol, Patent application 107711 E, 2014.

[53] N. Gama, L.C. Costa, V. Amaral, A. Ferreira, A. Barros-Timmons, Insights into the physical properties of biobased polyurethane/expanded graphite composite foams, Compos. Sci. Technol. 138 (2017) 24–31.

[54] N. V. Gama, R. Silva, M. Costa, A. Barros-Timmons, A. Ferreira, Statistical evaluation of the effect of formulation on the properties of crude glycerol polyurethane foams, Polym. Test. 56 (2016) 200–206.

[55] J.P.S. Aniceto, I. Portugal, C.M. Silva, Biomass-based polyols through oxypropylation reaction, ChemSusChem. 5 (2012) 1358–68.

[56] N. Zhao, Polycondensation reaction and its mechanism during lignocellulosic liquefaction by an acid catalyst: a review, 13 (2011) 71–79.

[57] M. Belgacem, A. Gandini, Monomers, Polymers and Composites from Renewable Resources, Elsevier, 2008.

[58] A. Gandini, C. Pinto, J.J. Costa, N.C. Pascoal, Process for the production of liquid poliols of renewable origin by the liquefaction of agro-forestry and agro-food biomass, 2010.

[59] G. Lammers, E.J. Stamhuis, A.A.C.M. Beenackers, Kinetics of the hydroxypropylation of potato starch in aqueous solution, Ind. Eng. Chem. Res. 32 (1993) 835–842.

[60] A. Gandini, M.N. Belgacem, Recent Contributions to the Preparation of Polymers Derived from Renewable Resources, J. Polym. Environ. 10 (2002) 105–114.

[61] C. Pavier, A. Gandini, Oxypropylation of sugar beet pulp. 1. Optimisation of the reaction, Ind. Crops Prod. 12 (2000) 1–8.

[62] C. Pavier, A. Gandini, Oxypropylation of sugar beet pulp. 2. Separation of the grafted pulp from the propylene oxide homopolymer, Carbohydr. Polym. 42 (2000) 13–17.

[63] C. Pavier, A. Gandini, Urethanes and polyurethanes from oxypropylated sugar beet pulp I . Kinetic study in solution, Eur. Polym. J. 36 (2000) 1653–1658.

[64] M. Evtiouguina, A. Barros-Timmons, J.J. Cruz-Pinto, C.P. Neto, M.N. Belgacem, A. Gandini, Oxypropylation of cork and the use of the ensuing polyols in polyurethane formulations, Biomacromolecules. 3 (2002) 57–62.

[65] M. Evtiouguina, A. Gandini, C.P. Neto, N.M. Belgacem, Urethanes and polyurethanes based on oxypropylated cork: 1. Appraisal and reactivity of products, Polym. Int. 50 (2001) 1150–1155.

[66] A. Gandini, C. Pascoal Neto, A.J.D. Silvestre, Suberin: A promising renewable resource for novel macromolecular materials, Prog. Polym. Sci. 31 (2006) 878–892.

[67] N. Cordeiro, M.N. Belgacem, A. Gandini, C. Pascoal Neto, Urethanes and polyurethanes from suberin 2: synthesis and characterization, Ind. Crops Prod. 10 (1999) 1–10.

[68] N. Cordeiro, M.N. Belgacem, A. Gandini, C.P. Neto, Urethanes and polyurethanes from suberin: 1. Kinetic study, Ind. Crops Prod. 6 (1997) 163–167.

[69] M. Evtiouguina, A. Margarida Barros, J.J. Cruz-Pinto, C. Pascoal Neto, N. Belgacem, C. Pavier, et al., The oxypropylation of cork residues: preliminary results, Bioresour. Technol. 73 (2000) 187–189.

[70] S. Fernandes, C.S.R. Freire, C.P. Neto, A. Gandini, The bulk oxypropylation of chitin and chitosan and the characterization of the ensuing polyols, Green Chem. 10 (2008) 93–97.

[71] A.J. de Menezes, D. Pasquini, A.A.S. Curvelo, A. Gandini, Novel thermoplastic materials based on the outer-shell oxypropylation of corn starch granules, Biomacromolecules. 8 (2007) 2047–50.

[72] R. Briones, L. Serrano, R. Ben Younes, I. Mondragon, J. Labidi, Polyol production by chemical modification of date seeds, Ind. Crops Prod. 34 (2011) 1035–1040.

[73] L. Serrano, M.G. Alriols, R. Briones, I. Mondragón, J. Labidi, Oxypropylation of Rapeseed Cake Residue Generated in the Biodiesel Production Process, Ind. Eng. Chem. Res. 49 (2010) 1526–1529.

[74] M. Matos, M.F. Barreiro, A. Gandini, Olive stone as a renewable source of biopolyols, Ind. Crops Prod. 32 (2010) 7–12.

[75] H. Nadji, C. Bruzzèse, M.N. Belgacem, A. Benaboura, A. Gandini, Oxypropylation of Lignins and Preparation of Rigid Polyurethane Foams from the Ensuing Polyols, Macromol. Mater. Eng. 290 (2005) 1009–1016.

[76] J.S. Amaral, M. Sepúlveda, C. a. Cateto, I.P. Fernandes, A.E. Rodrigues, M.N. Belgacem, et al., Fungal degradation of lignin-based rigid polyurethane foams, Polym. Degrad. Stab. 97 (2012) 2069–2076.

[77] X. Pan, J.N. Saddler, Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam, Biotechnol. Biofuels. 6 (2013) 12.

[78] Y. Li, A.J. Ragauskas, Kraft Lignin-Based Rigid Polyurethane Foam, J. Wood Chem. Technol. 32 (2012) 210–224.

[79] J. D'Souza, B. George, R. Camargo, N. Yan, Synthesis and characterization of bio-polyols through the oxypropylation of bark and alkaline extracts of bark, Ind. Crops Prod. 76 (2015) 1–11.

[80] A. Arbenz, A. Frache, F. Cuttica, L. Avérous, Advanced biobased and rigid foams, based on urethane-modified isocyanurate from oxypropylated gambier tannin polyol, Polym. Degrad. Stab. 132 (2016) 62–68.

[81] Y. Yan, M. Hu, Z. Wang, Kinetic study on the liquefaction of corn stalk in polyhydric alcohols, Ind. Crops Prod. 32 (2010) 349–352.

[82] Y. Jin, X. Ruan, X. Cheng, Q. Lü, Liquefaction of lignin by polyethyleneglycol and glycerol, Bioresour. Technol. 102 (2011) 3581–3.

[83] S. Hu, X. Luo, Y. Li, Polyols and polyurethanes from the liquefaction of lignocellulosic biomass, ChemSusChem. 7 (2014) 66–72.

[84] S. Hu, Y. Li, Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol for the production of polyols and polyurethane foams, Bioresour. Technol. 161 (2014) 410–5.

[85] E.M. Hassan, N. Shukry, Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues, Ind. Crops Prod. 27 (2008) 33–38.

[86] M. Niu, G. Zhao, M.H. Alma, Polycondensation reaction and its mechanism during lignocellulosic liquefaction by an acid catalyst: a review, For. Stud. China. 13 (2011) 71–79.

[87] H. Wang, H.-Z. Chen, A novel method of utilizing the biomass resource: Rapid liquefaction of wheat straw and preparation of biodegradable polyurethane foam (PUF), J. Chinese Inst. Chem. Eng. 38 (2007) 95–102.

[88] A.M.C. Yona, F. Budija, B. Kričej, A. Kutnar, M. Pavlič, P. Pori, et al., Production of biomaterials from cork: Liquefaction in polyhydric alcohols at moderate temperatures, Ind. Crops Prod. 54 (2014) 296–301.

[89] B. Soares, N.V. Gama, C.S.R. Freire, A. Barros-Timmons, I. Brandão, R. Silva, et al., Ecopolyol Production from Industrial Cork Powder via Acid Liquefaction Using Polyhydric Alcohols, ACS Sustain. Chem. Eng. 2 (2014) 846–854.

[90] N. V Gama, B. Soares, C.S. Freire, R. Silva, I. Brandão, C.P. Neto, et al., Rigid polyurethane foams derived from cork liquefied at atmospheric pressure, Polym. Int. 60 (2014) 250–257.

[91] T. Wang, D. Li, L. Wang, J. Yin, X.D. Chen, Z. Mao, Effects of CS/EC ratio on structure and properties of polyurethane foams prepared from untreated liquefied corn stover with PAPI, Chem. Eng. Res. Des. 86 (2008) 416–421.

[92] T. Wang, L. Zhang, D. Li, J. Yin, S. Wu, Z. Mao, Mechanical properties of polyurethane foams prepared from liquefied corn stover with PAPI, Bioresour. Technol. 99 (2008) 2265–8.

[93] L. Ye, J. Zhang, J. Zhao, S. Tu, Liquefaction of bamboo shoot shell for the production of polyols, Bioresour. Technol. 153 (2014) 147–53.

[94] L.-L. Gao, Y.-H. Liu, H. Lei, H. Peng, R. Ruan, Preparation of semirigid polyurethane foam with liquefied bamboo residues, J. Appl. Polym. Sci. 116 (2010) 1694–1699.

[95] M.S. Fidan, M.H. Alma, Preparation and characterization of biodegradable rigid polyurethane foams from the liquified eucalyptus and pine woods, Wood Res. 59 (2014) 97–108.

[96] A.A. Abdel Hakim, M. Nassar, A. Emam, M. Sultan, Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol, Mater. Chem. Phys. 129 (2011) 301–307.

[97] B. Soares, N.V. Gama, C.S.R. Freire, A. Barros-Timmons, I. Brandão, R. Silva, et al., Spent Coffee Grounds as a Renewable Source for Ecopolyols Production, J. Chem. Technol. Biotechnol. 64 (2014) 250–275.

[98] R.C. Sun, Cereal straw as a resource for sustainable biomaterials and biofuels, Elsevier, 2010.

[99] M. Nasar, A. Emam, M. Sultan, A.A.A. Hakim, Optimization and Characterization of Sugar-cane Bagasse Liquefaction Process, Indian J. Sci. Technol. 3 (2010) 207–212.

[100] E. Sharmin, F. Zafar, S. Ahmad, Seed Oil Based Polyurethanes: An Insight, Intech, India, 2012.

[101] O. S. Ogunfeyitimi, A.O. Okewale, P.K. Igbokwe, The Use of Castor Oil as a Reactive Monomer in Synthesis of Flexible Polyurethane Foam, Int. J. Multidiscip. Sci. Eng. 3 (2012) 10–14.

[102] A. Saralegi, M.L. Gonzalez, A. Valea, A. Eceiza, M.A. Corcuera, The role of cellulose nanocrystals in the improvement of the shape-memory properties of castor oil-based segmented thermoplastic polyurethanes, Compos. Sci. Technol. 92 (2014) 27–33.

[103] H. Yeganeh, M.R. Mehdizadeh, Synthesis and properties of isocyanate curable millable polyurethane elastomers based on castor oil as a renewable resource polyol, Eur. Polym. J. 40 (2004) 1233–1238.

[104] C. Sharma, S. Kumar, a. R. Unni, V.K. Aswal, S.K. Rath, G. Harikrishnan, Foam stability and polymer phase morphology of flexible polyurethane foams synthesized from castor oil, J. Appl. Polym. Sci. 131 (2014) 40668–40676.

[105] M. Spontón, N. Casis, P. Mazo, B. Raud, A. Simonetta, L. Ríos, et al., Biodegradation study by Pseudomonas sp. of flexible polyurethane foams derived from castor oil, Int. Biodeterior. Biodegradation. 85 (2013) 85–94.

[106] L. Zhang, M. Zhang, L. Hu, Y. Zhou, Synthesis of rigid polyurethane foams with castor oil-based flame retardant polyols, Ind. Crops Prod. 52 (2014) 380–388.

[107] H. Yeganeh, P. Hojati-Talemi, Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol), Polym. Degrad. Stab. 92 (2007) 480–489.

[108] M. Zhang, H. Pan, L. Zhang, L. Hu, Y. Zhou, Study of the mechanical, thermal properties and flame retardancy of rigid polyurethane foams prepared from modified castor-oil-based polyols, Ind. Crops Prod. 59 (2014) 135–143.

[109] L. Zhang, M. Zhang, Y. Zhou, L. Hu, The study of mechanical behavior and flame retardancy of castor oil phosphate-based rigid polyurethane foam composites containing expanded graphite and triethyl phosphate, Polym. Degrad. Stab. 98 (2013) 2784–2794.

[110] M.A. Corcuera, L. Rueda, B. Fernandez d'Arlas, A. Arbelaiz, C. Marieta, I. Mondragon, et al., Microstructure and properties of polyurethanes derived from castor oil, Polym. Degrad. Stab. 95 (2010) 2175–2184.

[111] P.O. Ikeh, Comparative Analysis of Flame Characteristics of Castor Oil and Some Other Inorganic Flame Retardants Used in Polyurethane Foam Systems Keywords: Flame retardants; Polyurethane; Ignition time; Form; Add-on, Niger. J. Basic Appl. Sci. 19 (2011) 55–63.

[112] Z.S. Petrović, I. Cvetković, Vegetable Oil-Based Hyperbranched Polyols in Flexible Foams, Contemp. Mater. 1 (2012) 63–71.

[113] K.H. Badri, Biobased Polyurethane from Palm Kernel Oil-Based Polyol, Intech, 2012.

[114] H. Pawlik, A. Prociak, Influence of Palm Oil-Based Polyol on the Properties of Flexible Polyurethane Foams, J. Polym. Environ. 20 (2011) 438–445.

[115] R. Tanaka, S. Hirose, H. Hatakeyama, Preparation and characterization of polyurethane foams using a palm oil-based polyol, Bioresour. Technol. 99 (2008) 3810–3816.

[116] S. Chuayjuljit, T. Sangpakdee, Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam, J. Met. Mater. Miner. 17 (2007) 17–23.

[117] B. Tamami, S. Sohn, G.L. Wilkes, Incorporation of Carbon Dioxide into Soybean Oil and Subsequent Preparation and Studies of Nonisocyanate Polyurethane Networks, J. Appl. Polym. Sci. 92 (2004) 883–891.

[118] M.F. Sonnenschein, B.L. Wendt, Design and formulation of soybean oil derived flexible polyurethane foams and their underlying polymer structure/property relationships, Polymer. 54 (2013) 2511–2520.

[119] R. Gu, S. Konar, M. Sain, Preparation and Characterization of Sustainable Polyurethane Foams from Soybean Oils, J. Am. Oil Chem. Soc. 89 (2012) 2103–2111.

[120] T.W. Pechar, S. Sohn, G.L. Wilkes, S. Ghosh, C.E. Frazier, A. Fornof, et al., Characterization and Comparasion of Polyurethane Networks Prepared Using Soybean-Based Polyols, J. Appl. Polym. Sci. 101 (2006) 1432–1443.

[121] L. Zhang, H.K. Jeon, J. Malsam, R. Herrington, C.W. Macosko, Substituting soybean oil-based polyol into polyurethane flexible foams, Polymer. 48 (2007) 6656–6667.

[122] J. John, M. Bhattacharya, R.B. Turner, Characterization of polyurethane foams from soybean oil, J. Appl. Polym. Sci. 86 (2002) 3097–3107.

[123] A.A. Beltran, L.A. Boyaca, Preparation of oleochemical polyols derived from soybean oil, Lat. Am. Appl. Res. 74 (2011) 69–74.

[124] X. Luo, A. Mohanty, M. Misra, Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane, Ind. Crops Prod. 47 (2013) 13–19.

[125] H. Bakhshi, H. Yeganeh, S. Mehdipour-Ataei, M.A. Shokrgozar, A. Yari, S.N. Saeedi-Eslami, Synthesis and characterization of antibacterial polyurethane coatings from quaternary ammonium salts functionalized soybean oil based polyols, Mater. Sci. Eng. C. 33 (2013) 153–164.

[126] A. Guo, I. Javni, Z. Petrovic, Rigid Polyurethane Foams Based on Soybean Oil, J. Appl. Polym. Sci. 77 (1999) 467–473.

[127] S. Hu, C. Wan, Y. Li, Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw, Bioresour. Technol. 103 (2012) 227–33.

[128] A. Fridrihsone, U. Stirna, B. Lazdiņa, M. Misāne, D. Vilsone, Characterization of polyurethane networks structure and properties based on rapeseed oil derived polyol, Eur. Polym. J. 49 (2013) 1204–1214.

[129] C. Philipp, S. Eschig, Waterborne polyurethane wood coatings based on rapeseed fatty acid methyl esters, Prog. Org. Coatings. 74 (2012) 705–711.

[130] X. Kong, G. Liu, J.M. Curtis, Novel polyurethane produced from canola oil based poly(ether ester) polyols: Synthesis, characterization and properties, Eur. Polym. J. 48 (2012) 2097–2106.

[131] V. Ribeiro da Silva, M.A. Mosiewicki, M.I. Yoshida, M. Coelho da Silva, P.M. Stefani, N.E. Marcovich, Polyurethane foams based on modified tung oil and reinforced with rice husk ash II: Mechanical characterization, Polym. Test. 32 (2013) 665–672.

[132] N. Karak, Vegetable oil-based polymers - properties, processing and applications, Woodhead Publishing, Oxford, Cambridge, 2012.

[133] L. Zhang, M. Zhang, L. Hu, Y. Zhou, Synthesis of rigid polyurethane foams with castor oil-based flame retardant polyols, Ind. Crops Prod. 52 (2014) 380–388.

[134] M. Kurańska, A. Prociak, The influence of rapeseed oil-based polyols on the foaming process of rigid polyurethane foams, Ind. Crops Prod. 89 (2016) 182–187.

[135] H.W. Tan, A.R. Abdul Aziz, M.K. Aroua, Glycerol production and its applications as a raw material: A review, Renew. Sustain. Energy Rev. 27 (2013) 118–127.

[136] S. Authayanun, A. Arpornwichanop, W. Paengjuntuek, S. Assabumrungrat, Thermodynamic study of hydrogen production from crude glycerol autothermal reforming for fuel cell applications, Int. J. Hydrogen Energy. 35 (2010) 6617–6623.

[137] X. Liu, P.R. Jensen, M. Workman, Bioconversion of crude glycerol feedstocks into ethanol by Pachysolen tannophilus, Bioresour. Technol. 104 (2012) 579–586.

[138] Y. Liu, C.M.J. Koh, L. Ji, Bioconversion of crude glycerol to glycolipids in Ustilago maydis, Bioresour. Technol. 102 (2011) 3927–3933.

[139] M. Ayoub, A.Z. Abdullah, Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry, Renew. Sustain. Energy Rev. 16 (2012) 2671–2686.

[140] P. Anand, S. Yadav, V. Kumar, K. Dutt, R.K. Saxena, A Path to Economic Viability for the Biodiesel Industry: Production of 1,3-Propanediol from Crude Glycerol, J. Biotechnol. 150 (2010) 370–370.

[141] A. Wolfson, G. Litvak, C. Dlugy, Y. Shotland, D. Tavor, Employing crude glycerol from biodiesel production as an alternative green reaction medium, Ind. Crops Prod. 30 (2009) 78–81.

[142] V. Sricharoenchaikul, D. Atong, Fuel Gas Generation from Thermochemical Conversion of Crude Glycerol Mixed with Biomass Wastes, Energy Procedia. 14 (2012) 1286–1291.

[143] J.M.B. Ezequiel, J.B.D. Sancanari, O.R. Machado Neto, Z.F. da Silva, M.T.C. Almeida, D.A.V. Silva, et al., Effects of high concentrations of dietary crude glycerin on dairy cow productivity and milk quality, J. Dairy Sci. 98 (2015) 8009–8017.

[144] L. Liu, M. Zong, Y. Hu, N. Li, W. Lou, H. Wu, Efficient microbial oil production on crude glycerol by Lipomyces starkeyi AS 2.1560 and its kinetics, Process Biochem. 58 (2017) 230–238.

[145] P. Kaewwisetkul, L. Simasatitkul, A. Arpornwichanop, Design and optimization of dimethyl ether production from crude glycerol in a reactive distillation, Chem. Eng. Process. Process Intensif. 117 (2017) 80–88.

[146] V.K. Garlapati, U. Shankar, A. Budhiraja, Bioconversion technologies of crude glycerol to value added industrial products, Biotechnol. Reports. 9 (2016) 9–14.

[147] A. Hejna, P. Kosmela, K. Formela, Ł. Piszczyk, J.T. Haponiuk, Potential applications of crude glycerol in polymer technology–Current state and perspectives, Renew. Sustain. Energy Rev. 66 (2016) 449–475.

[148] R. Dhabhai, E. Ahmadifeijani, A.K. Dalai, M. Reaney, Purification of crude glycerol using a sequential physico-chemical treatment, membrane filtration, and activated charcoal adsorption, Sep. Purif. Technol. 168 (2016) 101–106.

[149] X. Luo, X. Ge, S. Cui, Y. Li, Value-added processing of crude glycerol into chemicals and polymers, Bioresour. Technol. 215 (2016) 144–154.

[150] P.S. Kong, M.K. Aroua, W.M.A.W. Daud, Conversion of crude and pure glycerol into derivatives: A feasibility evaluation, Renew. Sustain. Energy Rev. 63 (2016) 533–555.

[151] S. Hu, Y. Li, Polyols and polyurethane foams from base-catalyzed liquefaction of lignocellulosic biomass by crude glycerol: Effects of crude glycerol impurities, Ind. Crops Prod. 57 (2014) 188–194.

[152] Y. Li, Y. Zhou, A. Lubguban, Methods for producing polyols and polyurethanes, Patent US20110054059 A1, 2011.

[153] Y. Li, Y. Zhou, A. Lubguban, Methods for producing polyols and polyurethanes, Patent WO 2011028645 A1, 2011.

[154] Y. Li, Y. Zhou, Methods for producing polyols using crude glycerin, Patent US 8022257 B2, 2011.

[155] X. Luo, S. Hu, X. Zhang, Y. Li, Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams, Bioresour. Technol. 139 (2013) 323–329.

[156] E.F. Gómez, X. Luo, C. Li, F.C. Michel, Y. Li, Biodegradability of crude glycerol-based polyurethane foams during composting, anaerobic digestion and soil incubation, Polym. Degrad. Stab. 102 (2014) 195–203.

[157] C. Li, X. Luo, T. Li, X. Tong, Y. Li, Polyurethane foams based on crude glycerol-derived biopolyols: One-pot preparation of biopolyols with branched fatty acid ester chains and its effects on foam formation and properties, Polymer. 55 (2014) 6529–6538.

[158] P. Guide, MDI and TDI: Safety, Health and the Environment. A Source Book and Practical Guide, John Wiley & Sons Ltd, 2003.

[159] L. Shufen, J. Zhi, Y. Kaijun, Y. Shuqin, W.K. Chow, Studies on the Thermal Behavior of Polyurethanes, Polym. Plast. Technol. Eng. 45 (2006) 95–108.

[160] R.J. Harris, ANOVA : an analysis of variance primer, F.E. Peacock Publishers, 1994.

[161] V. Popescu, A. Muresan, G. Popescu, M. Balan, M. Dobromir, Ethyl chitosan synthesis and quantification of the effects acquired after grafting it on a cotton fabric, using ANOVA statistical analysis, Carbohydr. Polym. 138 (2016) 94–105.

[162] A. Qasim, S. Nisar, A. Shah, M.S. Khalid, M.A. Sheikh, Optimization of process parameters for machining of AISI-1045 steel using Taguchi design and ANOVA, Simul. Model. Pract. Theory. 59 (2015) 36–51.

[163] B. Tousignant, K. Sirois, A.M. Achim, E. Massicotte, P.L. Jackson, A comprehensive assessment of social cognition from adolescence to adulthood, Cogn. Dev. 43 (2017) 214–223.

[164] S.R. Sain, D. Nychka, L. Mearns, Functional ANOVA and regional climate experiments: a statistical analysis of dynamic downscaling, Environmetrics. 22 (2011) 700–711.

[165] C. I.R, Castable Polyurethane Elastomers, CRC Press, 2008.

[166] Thermal Conductivity of common Materials and Gases, Eng. ToolBox. (2017). https://www.engineeringtoolbox.com/thermal-conductivity-d_429.html (accessed June 14, 2017).

[167] R.M.E. Diamant, Thermal and Acoustic Insulation, Elsevier, 1986.

[168] R. Boetes, Doctoral thesis - Heat transfer reduction in closed cell polyurethane foams, Delft university, 1984.

[169] A. Cunningham, N.C. Hilyard, Physical behaviour of polymeric foams — an overview, Springer Netherlands, Dordrecht, 1994.

[170] C. Alkan, E. Günther, S. Hiebler, Ö.F. Ensari, D. Kahraman, Polyurethanes as solid–solid phase change materials for thermal energy storage, Sol. Energy. 86 (2012) 1761–1769.

[171] N. Sarier, E. Onder, Thermal characteristics of polyurethane foams incorporated with phase change materials, Thermochim. Acta. 454 (2007) 90–98.

[172] N. Sarier, E. Onder, Thermal insulation capability of PEG-containing polyurethane foams, Thermochim. Acta. 475 (2008) 15–21.

[173] M. Rostamizadeh, M. Khanlarkhani, S. Mojtaba Sadrameli, Simulation of energy storage system with phase change material (PCM), Energy Build. 49 (2012) 419–422.

[174] C. Yang, L. Fischer, S. Maranda, J. Worlitschek, Rigid polyurethane foams incorporated with phase change materials: A state-of-the-art review and future research pathways, Energy Build. 87 (2015) 25–36. doi:10.1016/j.enbuild.2014.10.075.

[175] M. You, X.X. Zhang, W. Li, X.C. Wang, Effects of MicroPCMs on the fabrication of MicroPCMs/polyurethane composite foams, Thermochim. Acta. 472 (2008) 20–24.

[176] A. Tinti, A. Tarzia, A. Passaro, R. Angiuli, Thermographic analysis of polyurethane foams integrated with phase change materials designed for dynamic thermal insulation in refrigerated transport, Appl. Therm. Eng. 70 (2014) 201–210.

[177] C. Amaral, R. Vicente, P.A.A.P. Marques, A. Barros-Timmons, Phase change materials and carbon nanostructures for thermal energy storage: A literature review, Renew. Sustain. Energy Rev. 79 (2017) 1212–1228.

[178] C.R. Abujas, A. Jové, C. Prieto, M. Gallas, L.F. Cabeza, Performance comparison of a group of thermal conductivity enhancement methodology in phase change material for thermal storage application, Renew. Energy. 97 (2016) 434–443.

[179] Q. Meng, J. Hu, A poly(ethylene glycol)-based smart phase change material, Sol. Energy Mater. Sol. Cells. 92 (2008) 1260–1268.

[180] W. Li, D. Zhang, T. Zhang, T. Wang, D. Ruan, D. Xing, et al., Study of solid–solid phase change of (n-CnH2n+1NH3)2MCl4 for thermal energy storage, Thermochim. Acta. 326 (1999) 183–186.

[181] G.Z. Ke, H.F. Xie, R.P. Ruan, W.D. Yu, Preparation and performance of porous phase change polyethylene glycol/polyurethane membrane, Energy Convers. Manag. 51 (2010) 2294–2298.

[182] Q. Cao, P. Liu, Hyperbranched polyurethane as novel solid–solid phase change material for thermal energy storage, Eur. Polym. J. 42 (2006) 2931–2939.

[183] P. Xi, Y. Duan, P. Fei, L. Xia, R. Liu, B. Cheng, Synthesis and thermal energy storage properties of the polyurethane solid–solid phase change materials with a novel tetrahydroxy compound, Eur. Polym. J. 48 (2012) 1295–1303.

[184] M. You, X. Zhang, X. Wang, L. Zhang, W. Wen, Effects of type and contents of microencapsuled n-alkanes on properties of soft polyurethane foams, Thermochim. Acta. 500 (2010) 69–75.

[185] N. Sarier, E. Onder, Organic phase change materials and their textile applications: An overview, Thermochim. Acta. 540 (2012) 7–60.

[186] P. Xi, L. Xia, P. Fei, D. Zhang, B. Cheng, Preparation and performance of a novel thermoplastics polyurethane solid–solid phase change materials for energy storage, Sol. Energy Mater. Sol. Cells. 102 (2012) 36–43.

[187] A. Sarı, C. Alkan, A. Karaipekli, O. Uzun, Microencapsulated n-octacosane as phase change material for thermal energy storage, Sol. Energy. 83 (2009) 1757–1763.

[188] M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change energy storage: materials and applications, Energy Convers. Manag. 45 (2004) 1597–1615.

[189] M. El Hasnaoui, A. Triki, M.P.F. Graça, M.E. Achour, L.C. Costa, M. Arous, Electrical conductivity studies on carbon black loaded ethylene butylacrylate polymer composites, J. Non. Cryst. Solids. 358 (2012) 2810–2815.

[190] D.K. Chattopadhyay, D.C. Webster, Thermal stability and flame retardancy of polyurethanes, Prog. Polym. Sci. 34 (2009) 1068–1133.

[191] ISO 834-11:2014 - Fire resistance tests, (2014).

[192] EN 13501-2 - Fire classification of construction products and buildings elements, (2007) 134. http://standards.globalspec.com/std/1399872/uni-en-13501-2 (accessed June 09, 2017).

[193] W. Zatorski, Z.K. Brzozowski, A. Kolbrecki, New developments in chemical modification of fire-safe rigid polyurethane foams, Polym. Degrad. Stab. 93 (2008) 2071–2076.

[194] L. Ye, X.Y. Meng, X. Ji, Z.M. Li, J.H. Tang, Synthesis and characterization of expandable graphite–poly(methyl methacrylate) composite particles and their application to flame retardation of rigid polyurethane foams, Polym. Degrad. Stab. 94 (2009) 971–979.

[195] M. Modesti, A. Lorenzetti, Flame retardancy of polyisocyanurate-polyurethane foams: Use of different charring agents, Polym. Degrad. Stab. 78 (2002) 341–347.

[196] M. Modesti, A. Lorenzetti, F. Simioni, M. Checchin, Influence of different flame retardants on fire behaviour of modified PIR/PUR polymers, Polym. Degrad. Stab. 74 (2001) 475–479.

[197] Y. Chung, Y. Kim, S. Kim, Flame retardant properties of polyurethane produced by the addition of phosphorous containing polyurethane oligomers (II), J. Ind. Eng. Chem. 15 (2009) 888–893.

[198] L. Qian, F. Feng, S. Tang, Bi-phase flame-retardant effect of hexa-phenoxy-cyclotriphosphazene on rigid polyurethane foams containing expandable graphite, Polymer. 55 (2014) 95–101.

[199] M. Modesti, A. Lorenzetti, Improvement on fire behaviour of water blown PIR–PUR foams: use of an halogen-free flame retardant, Eur. Polym. J. 39 (2003) 263–268.

[200] M. Kleiner, J. Tichy, Acoustics of small rooms, CRC Press, New York, 20114.

[201] D. Jahani, A. Ameli, P.U. Jung, M.R. Barzegari, C.B. Park, H. Naguib, Open-cell cavity-integrated injection-molded acoustic polypropylene foams, Mater. Des. 53 (2014) 20–28.

[202] N.N. Najib, Z.M. Ariff, A.A. Bakar, C.S. Sipaut, Correlation between the acoustic and dynamic mechanical properties of natural rubber foam: Effect of foaming temperature, Mater. Des. 32 (2011) 505–511.

[203] G. Ballou, Handbook for sound engineers, 4th ed., Focal Press, Amsterdam, 2008.

[204] C. Zhang, J. Li, Z. Hu, F. Zhu, Y. Huang, Correlation between the acoustic and porous cell morphology of polyurethane foam: Effect of interconnected porosity, Mater. Des. 41 (2012) 319–325.

[205] M. Cregut, M. Bedas, M.-J. Durand, G. Thouand, New insights into polyurethane biodegradation and realistic prospects for the development of a sustainable waste recycling process, Biotechnol. Adv. 31 (2013) 1634–1647.

[206] Y. Ohama, Disposal and Recycling of Organic and Polymeric Construction : Proceedings of the International RILEM Workshop., Spon Press, 1995.

[207] W. Yang, Q. Dong, S. Liu, H. Xie, L. Liu, J. Li, Recycling and Disposal Methods for Polyurethane Foam Wastes, Procedia Environ. Sci. 16 (2012) 167–175.

[208] K.M. Zia, H.N. Bhatti, I. Ahmad Bhatti, Methods for polyurethane and polyurethane composites, recycling and recovery: A review, React. Funct. Polym. 67 (2007) 675–692.

[209] O.B. Johnson, Method for continuous hydrolysis of polyurethane foam in restricted tubular reaction zone and recovery, US 4025559 A, 1977.

[210] K. Kanaya, S. Takahashi, Decomposition of polyurethane foams by alkanolamines, J. Appl. Polym. Sci. 51 (1994) 675–682.

[211] G. Behrendt, B.W. Naber, The chemical recycling of polyurethanes (Review), J. Univ. Chem. Technol. Metall. 44 (2009) 3–23.

[212] R.M. Machado, B.E. Farrell, Process for modifying the glycolysis reaction product of polyurethane scrap, US 5300530 A, 1994.

[213] M.H. Zdenek Krulis, Zdenek Horak, Hynek Benes, Method of recycling waste polyurethane foams, WO 2009024102 A2, 2009.

[214] C. a G. Quispe, C.J.R. Coronado, J. a. Carvalho, Glycerol: Production, consumption, prices, characterization and new trends in combustion, Renew. Sustain. Energy Rev. 27 (2013) 475–493. doi:10.1016/j.rser.2013.06.017.

[215] M.S. Ardi, M.K. Aroua, N.A. Hashim, Progress, prospect and challenges in glycerol purification process: A review, Renew. Sustain. Energy Rev. 42 (2015) 1164–1173. doi:10.1016/j.rser.2014.10.091.

[216] Solvay, Solvay to build bio-based Epichlorohydrin plant in China to serve largest market in the world, 2012. http://www.solvay.com/en/media/press_releases/20120611-epicerol-china.html (accessed October 04, 2016).

[217] C.A. Cateto, M.F. Barreiro, A.E. Rodrigues, M.N. Belgacem, Optimization Study of Lignin Oxypropylation in View of the Preparation of Polyurethane Rigid Foams, Ind. Eng. Chem. Res. 48 (2009) 2583–2589.

[218] O. Kwon, S. Yang, D. Kim, J. Park, Characterization of Polyurethane Foam Prepared by Using Starch as Polyol, J. Appl. Polym. Sci. 103 (2006) 1544–1553.

[219] S. Hu, C. Wan, Y. Li, Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw, Bioresour. Technol. 103 (2012) 227–33.

[220] B. Soares, N. Gama, C. Freire, A. Barros-Timmons, I. Brandão, R. Silva, et al., Ecopolyol Production from Industrial Cork Powder via Acid Liquefaction Using Polyhydric Alcohols, ACS Sustain. Chem. Eng. 2 (2014) 846–854.

[221] S. Hu, Y. Li, Polyols and polyurethane foams from acid-catalyzed biomass liquefaction by crude glycerol: Effects of crude glycerol impurities, Ind. Crops Prod. 57 (2014) 188–194.

[222] T. Newbold, D.M. Casper, Methods of preparing hydroxy functional vegetable oils, US 20060041156 A1, 2006.

[223] J.T. Garrett, R. Xu, J. Cho, J. Runt, Phase separation of diamine chain-extended poly(urethane) copolymers: FTIR spectroscopy and phase transitions, Polymer. 44 (2003) 2711–2719.

[224] D.T. Okamoto, S.L. Cooper, T.W. Root, Carbon-13 NMR investigation of a poly(urethane-urea) system, Macromolecules. 25 (1992) 1068–1073.

[225] F. Saint-Michel, L. Chazeau, J.-Y. Cavaillé, E. Chabert, Mechanical properties of high density polyurethane foams: I. Effect of the density, Compos. Sci. Technol. 66 (2006) 2700–2708.

[226] T.W. Pechar, S. Sohn, G.L. Wilkes, S. Ghosh, C.E. Frazier, A. Fornof, et al., Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols, J. Appl. Polym. Sci. 101 (2006) 1432–1443.

[227] Y. Xu, Z. Petrovic, S. Das, G.L. Wilkes, Morphology and properties of thermoplastic polyurethanes with dangling chains in ricinoleate-based soft segments, Polymer. 49 (2008) 4248–4258.

[228] J.W. Miller, Z. Tang, M.M. Maroto-valer, J.M. Andre, L. Listemann, P.L. Mcdaniel, et al., Thermal degradation behavior of rigid polyurethane foams prepared with different fire retardant concentrations and blowing agents, Polymer. 43 (2002) 6471–6479.

[229] P. Saavalainen, S. Kabra, E. Turpeinen, K. Oravisjärvi, G.D. Yadav, R.L. Keiski, et al., Sustainability Assessment of Chemical Processes: Evaluation of Three Synthesis Routes of DMC, J. Chem. 2015 (2015).

[230] L.C. Dias, A.R. Domingues, On multi-criteria sustainability assessment: Spider-gram surface and dependence biases, Appl. Energy. 113 (2014) 159–163.

[231] S. Kabasci, Bio-Based Plastics, John Wiley & Sons Ltd, Chichester, UK, 2013.

[232] L. Yu, Biodegradable polymer blends and composites from renewable resources, 2009.

[233] H. Fan, A. Tekeei, G.J. Suppes, F.-H. Hsieh, Physical Properties of Soy-Phosphate Polyol-Based Rigid Polyurethane Foams, Int. J. Polym. Sci. 2012 (2012) 1–8.

[234] H.C. Jung, S.C. Ryu, W.N. Kim, Y.-B. Lee, K.H. Choe, S.-B. Kim, Properties of rigid polyurethane foams blown by HCFC 141B and distilled water, J. Appl. Polym. Sci. 81 (2001) 486–493.

[235] H. Hatakeyema, N. Tanamachi, H. Matsumura, S. Hirose, T. Hatakeyama, Bio-based polyurethane composite foams with inorganic fillers studied by thermogravimetry, Thermochim. Acta. 431 (2005) 155–160.

[236] S.H. Kim, B.K. Kim, H. Lim, Effect of isocyanate index on the properties of rigid polyurethane foams blown by HFC 365mfc, Macromol. Res. 16 (2008) 467–472.

[237] H. Lim, Effects of silicon surfactant in rigid polyurethane foams, eXPRESS Polym. Lett. 2 (2008) 194–200.

[238] V. Ribeiro da Silva, M.A. Mosiewicki, M.I. Yoshida, M. Coelho da Silva, P.M. Stefani, N.E. Marcovich, Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis and physical chemical characterization, Polym. Test. 32 (2013) 438–445.

[239] K.H. Choe, D.S. Lee, W.J. Seo, W.N. Kim, Properties of Rigid Polyurethane Foams with Blowing Agents and Catalysts, Polym. J. 36 (2004) 368–373.

[240] J. Murphy, Factors Contributing to K-Factor Optimization with Ecomate blown foams, in: CPI 2007 Conf., 2007.

[241] D.H. Park, G.P. Park, S.H. Kim, W.N. Kim, Effects of isocyanate index and environmentally-friendly blowing agents on the morphological, mechanical, and thermal insulating properties of polyisocyanurate-polyurethane foams, Macromol. Res. 21 (2013) 852–859.

[242] V.V. Tyagi, D. Buddhi, PCM thermal storage in buildings: A state of art, Renew. Sustain. Energy Rev. 11 (2007) 1146–1166.

[243] J.F. Su, L.X. Wang, L. Ren, Synthesis of polyurethane microPCMs containing n-octadecane by interfacial polycondensation: Influence of styrene-maleic anhydride as a surfactant, Colloids Surfaces A Physicochem. Eng. Asp. 299 (2007) 268–275.

[244] J.C. Su, P.S. Liu, A novel solid–solid phase change heat storage material with polyurethane block copolymer structure, Energy Convers. Manag. 47 (2006) 3185–3191.

[245] N. Soares, A. Samagaio, R. Vicente, J. Costa, Numerical Simulation of a PCM Shutter for Buildings Space Heating During the Winter, 2011.

[246] M.S. A.A. Abdel Hakima, Mona Nassara, Aisha Emamb, Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol.pdf, Mater. Chem. Phys. (2011) 301–307.

[247] M. Thirumal, D. Khastgir, N.K. Singha, B.S. Manjunath, Y.P. Naik, Effect of expandable graphite on the properties of intumescent flame-retardant polyurethane foam, J. Appl. Polym. Sci. 110 (2008) 2586–2594.

[248] M. Valentini, F. Piana, J. Pionteck, F.R. Lamastra, F. Nanni, Electromagnetic properties and performance of exfoliated graphite (EG) – Thermoplastic polyurethane (TPU) nanocomposites at microwaves, Compos. Sci. Technol. 114 (2015) 26–33.

[249] Y. Li, J. Zou, S. Zhou, Y. Chen, H. Zou, M. Liang, et al., Effect of expandable graphite particle size on the flame retardant, mechanical, and thermal properties of water-blown semi-rigid polyurethane foam, J. Appl. Polym. Sci. 131 (2014).

[250] M.C. Saha, M.E. Kabir, S. Jeelani, Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles, Mater. Sci. Eng. A. 479 (2008) 213–222.

[251] C.K. Ranaweera, M. Ionescu, N. Bilic, X. Wan, P.K. Kahol, R.K. Gupta, Biobased Polyols Using Thiol-Ene Chemistry for Rigid Polyurethane Foams with Enhanced Flame-Retardant Properties, J. Renew. Mater. (2017).

[252] N. Mills, Polymer Foams Handbook, Elsevier, 2007.

[253] A. Lorenzetti, B. Dittrich, B. Schartel, M. Roso, M. Modesti, Expandable graphite in polyurethane foams: The effect of expansion volume and intercalants on flame retardancy, J. Appl. Polym. Sci. 134 (2017) 45173.

[254] M. Kirpluks, U. Cabulis, A. Avots, Flammability of Bio-Based Rigid Polyurethane Foam as Sustainable Thermal Insulation Material, in: Insul. Mater. Context Sustain., InTech, 2016.

[255] A. Hejna, M. Kirpluks, P. Kosmela, U. Cabulis, J. Haponiuk, Ł. Piszczyk, The influence of crude glycerol and castor oil-based polyol on the structure and performance of rigid polyurethane-polyisocyanurate foams, Ind. Crops Prod. 95 (2017) 113–125.

[256] S.E. Gustafsson, Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials, Rev. Sci. Instrum. 62 (1991) 797–804.

[257] ISO 5660-1:2015 Preview Reaction to fire tests - Heat release, smoke production and mass loss rate - Part 1: Heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement), 2015.

[258] N. Gama, R. Silva, A.P.O. Carvalho, A. Ferreira, A. Barros-Timmons, Sound absorption properties of polyurethane foams derived from crude glycerol and liquefied coffee grounds polyol, Polym. Test. 62 (2017) 13–22.

[259] N. V Gama, B. Soares, C.S. Freire, R. Silva, A. Ferreira, A. Barros-Timmons, Effect of unrefined crude glycerol composition on the properties of polyurethane foams, J. Cell. Plast. (2017). doi:10.1177/0021955X17732304.

[260] G. Harikrishnan, S.N. Singh, E. Kiesel, C.W. Macosko, Nanodispersions of carbon nanofiber for polyurethane foaming, Polymer. 51 (2010) 3349–3353.

[261] Y. Zhang, G. Zou, S.K. Doorn, H. Htoon, L. Stan, M.E. Hawley, et al., Tailoring the morphology of carbon nanotube arrays: from spinnable forests to undulating foams., ACS Nano. 3 (2009) 2157–62.

[262] S. Desai, J. Njuguna, Enhancement of thermal conductivity of materials using different forms of natural graphite, IOP Conf. Ser. Mater. Sci. Eng. 40 (2012) 012017.

[263] D.R. Lide, H.P.R. Frederikse, CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data, CRC Press, 1993.

[264] Y. Jin, Q. Wan, Y. Ding, PCMs Heat Transfer Performance Enhancement with Expanded Graphite and its Thermal Stability, Procedia Eng. 102 (2015) 1877–1884.

[265] J. Jarosinski, B. Veyssiere, Combustion phenomena: selected mechanisms of flame formation, propagation, and extinction, CRC Press, 2009.

[266] M. Modesti, A. Lorenzetti, Halogen-free flame retardants for polymeric foams, Polym. Degrad. Stab. 78 (2002) 167–173.

[267] J. Eapen, R. Krishna, T.D. Burchell, K.L. Murty, Early Damage Mechanisms in Nuclear Grade Graphite under Irradiation, Mater. Res. Lett. 2 (2014) 43–50.

[268] H. Wang, Y.H. Hu, Effect of Oxygen Content on Structures of Graphite Oxides, Ind. Eng. Chem. Res. 50 (2011) 6132–6137.

[269] R. Del Rey, J. Alba, J.P. Arenas, V.J. Sanchis, An empirical modelling of porous sound absorbing materials made of recycled foam, Appl. Acoust. 73 (2012) 604–609.

[270] H. Benkreira, A. Khan, K.V. Horoshenkov, Sustainable acoustic and thermal insulation materials from elastomeric waste residues, Chem. Eng. Sci. 66 (2011) 4157–4171.

[271] Z. Li, M.J. Crocker, Effects of thickness and delamination on the damping in honeycomb–foam sandwich beams, J. Sound Vib. 294 (2006) 473–485.

[272] L. Bohnke, J. Beaujean, R. Albach, J. Li, S. Ling, Rigid polyurethane foams with high acoustic absorption, WO 2014153701 A1, 2013.

[273] A.E. Tiuc, H. Vermeşan, T. Gabor, O. Vasile, Improved Sound Absorption Properties of Polyurethane Foam Mixed with Textile Waste, Energy Procedia. 85 (2016) 559–565.

[274] S. Celebi, H. Kucuk, Acoustic Properties of Tea-Leaf Fiber Mixed Polyurethane Composites, Cell. Polym. 31 (2012) 241–255.

[275] G. Sung, S.K. Kim, J.W. Kim, J.H. Kim, Effect of isocyanate molecular structures in fabricating flexible polyurethane foams on sound absorption behavior, Polym. Test. 53 (2016) 156–164.

[276] N. V. Gama, R. Silva, C.P. Neto, A. Barros-Timmons, A. Ferreira, Acoustic and sound absorption properties of crude glycerol and coffee grounds derived polyurethane foams, in: A. Tiwari (Ed.), Adv. Mater. World Congr., Journal VBRI Press, 2015.

[277] X. Pan, J.N. Saddler, Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam., Biotechnol. Biofuels. 6 (2013) 12.

[278] M.A. Hakki, Polymeric Materials: New Research, Nova Publishers, 2005.

[279] G. Sung, J.H. Kim, Effect of high molecular weight isocyanate contents on manufacturing polyurethane foams for improved sound absorption coefficient, Korean J. Chem. Eng. (2017) 1–7.

[280] G. Sung, J.W. Kim, J.H. Kim, Fabrication of polyurethane composite foams with magnesium hydroxide filler for improved sound absorption, J. Ind. Eng. Chem. 44 (2016) 99–104.

[281] Y. Wang, C. Zhang, L. Ren, M. Ichchou, M.-A. Galland, O. Bareille, Influences of Rice Hull in Polyurethane Foam on Its Sound Absorption Characteristics, Polym. Compos. 34 (2013) 1847–1855.

[282] S.K. Kim, G. Sung, J.G. Gwon, J.H. Kim, Controlled phase separation in flexible polyurethane foams with diethanolamine cross-linker for improved sound absorption efficiency, Int. J. Precis. Eng. Manuf. Technol. 3 (2016) 367–373.

[283] N. Kino, G. Nakano, Y. Suzuki, Non-acoustical and acoustical properties of reticulated and partially reticulated polyurethane foams, Appl. Acoust. 73 (2012) 95–108.

[284] T.C. Hung, J.S. Huang, Y.W. Wang, K.Y. Lin, Inorganic polymeric foam as a sound absorbing and insulating material, Constr. Build. Mater. 50 (2014) 328–334.

[285] X. Wang, J. Eisenbrey, M. Zeitz, J.Q. Sun, Multi-stage regression analysis of acoustical properties of polyurethane foams, J. Sound Vib. 273 (2004) 1109–1117.