

Book of Abstracts: Cork in Science and Applications Conference 2023



universidade de aveiro theoria poiesis praxis INDAY

Title Book of Abstracts: Cork in Science and Applications Conference 2023 **Editors** Ricardo Alves de Sousa, Fábio Fernandes and Gabriel Serra

Publisher UA Editora Universidade de Aveiro

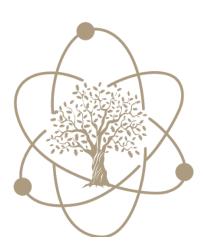
1st Edition – September 2023

ISBN 978-972-789-875-6

DOI https://doi.org/10.48528/p1yb-tj22

The sole responsibility for the content of this publication lies with the authors. © Authors. This work is licensed under a Creative Commons Attribution 4.0 International License.

BOOK OF ABSTRACTS



CORK IN SCIENCE AND APPLICATIONS 2023

Solverde Hotel & Spa 7 and 8 September 2023

http://corkscience.web.ua.pt/

Sponsored by



AMORIM CORK COMPOSITES

Supported by





JERK

Preface

It is with great pleasure that we welcome you to Vila Nova de Gaia to take part on the 4th edition of the Cork in Science and Applications Conference (CSA23). This event serves as a platform for scientists, researchers, industry professionals and enthusiasts from around the world to come together and delve into the fascinating world of cork.

Cork, with its unique properties and versatility, has been a subject of interest for centuries. Its natural resilience, low density, and excellent thermal and acoustic insulation properties have made it an invaluable material in various industries, ranging from architecture and design to aerospace and wine production. As we gather here today, we are presented with an exciting opportunity to explore the latest advancements in cork research and its wide-ranging applications.

This conference aims to foster collaboration, knowledge sharing, and innovation within the field of cork material science. We have curated a diverse program that encompasses a broad spectrum of topics, including cork extraction and processing techniques, cork characterization and properties, sustainable cork production, novel applications of cork in different industries, and the environmental impact of cork utilization.

Throughout the conference, you will have the chance to engage in thought-provoking discussions, attend insightful presentations, and connect with fellow professionals who share a common interest in cork. Our esteemed lineup of speakers comprises experts and pioneers in cork research, who will present their latest findings and shed light on emerging trends and future prospects within the field.

We would like to extend our sincere gratitude to the the dedicated contributors and our generous sponsors for their unwavering support in making this conference a reality.

Lastly, we encourage all participants to seize this opportunity to exchange knowledge, forge new partnerships, and contribute to the ever-growing body of research in cork material science. May this conference serve as a catalyst for innovative breakthroughs and sustainable solutions that will positively impact industries and the environment.

We wish you all a stimulating and rewarding experience at CSA23

Sincerely,

Ricardo Sousa, Fábio Fernandes and Gabriel Serra TEMA - University of Aveiro

Contents

VIRGIN CORK STRUCTURE OF QUERCUS VARIABILIS GROWING IN KOREA	4
MANUFACTURING OF CORK-STF COMPOSITES	7
CHARACTERISTICS OF CORK PAVING MATERIALS MADE BY PROCESSED CORK GRANULES	8
CONTRIBUTION TO THE CHARACTERIZATION OF CORKS' USE- LIFE	11
CORK USES IN ARCHITECTURE: BENEFITS FOR NZEB	17
MAGNESIUM-MODIFIED CORK BIOCHARS FOR THE REMOVAL OF PHOSPHATE FROM WATER	20
NEW HYBRID STRUCTURES BASED ON ALUMINIUM FOAMS AND CORK GRANULES	22
OXYGEN TRANSFER: THE CRUCIAL ROLE OF THE GLASS-CORK INTERFACE	24
INDUSTRIAL METHOD FOR NON-DESTRUCTIVELY SCREENING WINE CORK STOPPERS FOR 2,4,6- TRICHLOROANISOLE BELOW THE PERCEPTION THRESHOLD IN 2 SECONDS	27
LIQUID CRYSTALLINE SYSTEMS FROM CORK	29
MAGNETIC CORK-DERIVED POROUS COMPOSITES AS ADSORBENTS FOR WATER REMEDIATION TECHNOLOGIES	31
TCA SMART SENSOR FOR PROCESS CONTROL IN INDUSTRIAL SETTINGS	33
NEW INSIGHTS ON THE MECHANICAL PROPERTIES OF CORK IN COMPRESSION	35
IMPACT OF BOTTLENECK SHAPE ON CORK STOPPERS FUNCTIONAL PARAMETERS	37
INVESTIGATION OF DISCOLORATION FACTORS BY SELECTIVE EXTRACTION OF CORK COMPONEN OF QUERCUS VARIABILIS AND QUERCUS SUBER	
THERMOFORMING OF POLYLACTIC ACID AND CORK BIOCOMPOSITE SHEETS	46
INTER-TREE COMPETITION ANALYSIS IN SPANISH YOUNG CORK OAK PLANTATIONS	49
DETERMINATION OF MOISTURE CONTENT IN LOOSE CORK GRANULATE USING NEAR INFRARED SPECTROSCOPY (NIRS)	50
PRODUCTION OF OXIDE FILMS WITH UV-FILTERING PROPERTIES ON CORK AND RUBBER - SAFEGUARDING FROM UV RADIATION AND MECHANICAL WEAR	51
REPLACING POLYURETHANE IN AGGLOMERATED CORK USING A BIOBASED BINDER	53
PREDICTION OF SECONDARY CORK INDUSTRIAL QUALITY AND POROSITY BASED ON VIRGIN COR CHARACTERISTICS	
STUDY OF THE AROMATIC PROFILE OF QUERCUS SUBER L	57
STUDY OF CORK FROM <i>QUERCUS SUBER</i> WITH AND WITHOUT YELLOW SPOT: AROMATIC FRACTIC AND CELLULAR STRUCTURE	
THE INFLUENCE OF THE PRODUCTION PROCESS ON THE NATURAL CORK STOPPERS PERMEABILITAND ITS IMPACT ON STILL WINE AGING	
NOVEL SUSTAINABLE ALTERNATIVES FOR THE STUDY OF CHEMICAL COMPOSITION OF CORK	70
EVALUATION OF 2,4,6-TRICHLOROANISOLE CONTAMINATION IN CORK OAK FORESTS WITH TWO DIFFERENT MANAGEMENT MODELS	76
CORK FACADES: PERFORMANCE, ENVIRONMENTAL QUALITY AND PUBLIC PERCEPTION	78
REMEDIATION OF SOILS CONTAMINATED WITH PESTICIDES: SORPTION STUDIES OF LINDANE ON CORK	
THERMAL ANISOTROPY OF NATURAL CORK	89
INSIGHTS INTO CORK WEATHERING REGARDING COLOUR, CHEMICAL AND CELLULAR CHANGES.	95

PROMOTING THE DEVELOPMENT OF BLIND AND VISUALLY IMPAIRED CHILDREN THROUGH A CTOY	
PIEZORESISTIVE SENSORS SYNTHESIZED DIRECTLY ON CORK	100
CORK FACADES: PERFORMANCE, ENVIRONMENTAL QUALITY AND PUBLIC PERCEPTION	102
USE OF EXPANDED CORK IN HELMET FOR MICROMOBILITY	108
GEOPOLYMER COMPOSITES: A COMPARATIVE STUDY BETWEEN THE USE OF CORK AND SYNTH AGGREGATES	
CORK POWDER RESIDUES VALORISATION BY ADDITIVE MANUFACTURING	116
CORK STOPPER'S COATING DEPOSITION ANALYSIS USING AN INDUSTRIAL LIBS SYSTEM	121

D, Prasetia, B. D. Purusatama, J. H. Kim, J. H. Jang, S. Y. Park, and N. H. Kim



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

VIRGIN CORK STRUCTURE OF QUERCUS VARIABILIS GROWING IN KOREA

Denni Prasetia1, Byantara Darsan Purusatama2, Jong-Ho Kim1, Jae-Hyuk Jang3, Se- Yeong Park1, and Nam-Hun Kim1*

¹ Dept. of Forest Biomaterials Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon, 24341, Republic of Korea *Corresponding author: <u>kimnh@kangwon.ac.kr</u>

² Institute of Forest Science, Kangwon National University, Chuncheon 24341, Republic of Korea

³ FC Korea Land Co., Ltd., Seoul 07271, Republic of Korea

Keywords: dark-brown zone, lenticular channel, Quercus suber, Quercus variabilis, reproduction cork, sclereid, virgin cork

Abstract.

Cork is a natural product obtained from the outer bark of an oak species. Cork is light with low permeability to liquids, an excellent thermal insulator, shock absorption, and elastic compression due to a closed cellular structure with high suberin and lignin content. There are three types of cork: virgin cork, second cork, and reproduction cork. Virgin cork is the first cork layer produced by the original phellogen of the cork oak. The second cork is the new traumatic periderm produced by the regenerated phellogen after the removal of the virgin cork. The successive cork layers, grown after the removal of the second cork are reproduction corks (Pereira 2007).

In the Korean cork industry, the primary raw material for various products (e.g., wine stoppers, insulation boards, and surfacing products for pavements and sidewalls) is *Q. suber* reproduction

D, Prasetia, B. D. Purusatama, J. H. Kim, J. H. Jang, S. Y. Park, and N. H. Kim

cork imported from Portugal. As the demand for cork increases for the products, the Korean cork industry is trying to find alternative cork resources from domestic wood species. *Quercus variabilis* virgin cork is the only cork resource currently available in Korea. So far, there is still no study on the quality of the cork resources produced by the *Q. variabilis* grown in Korea. Therefore, to obtain basic data for further utilization of domestic cork resources, the qualitative and quantitative anatomical characteristics of *Q. variabilis* virgin cork grown in Korea were investigated by scanning electron microscopy and compared with those of commercial cork as *Quercus suber* reproduction cork from Portugal. The virgin cork of *Q. variabilis* was collected from three trees at breast height in the research forest of Kangwon National University (Chuncheon, Korea) (37°77'N, 127°81'E) and the reproduction cork of *Q. suber* from Portugal was provided by FC Korea Land Co., Ltd. (Seoul, Korea)

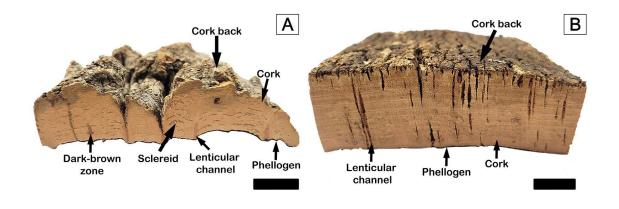


Figure 1. Virgin cork of Q. variabilis (A) and reproduction cork of Q. suber (B). Scale bars: 20 mm

In terms of qualitative features, dark-brown zones with sclereids were found only in *Q. variabilis* cork. *Q. variabilis* virgin cork showed a distinct growth ring boundary and an abrupt transition from earlycork to latecork with a few rows of latecork cells. *Q. suber* reproduction cork showed an indistinct growth ring with a gradual transition from one to two rows of latecork cells. In the earlycork, *Q. suber* showed mild corrugation, while *Q. variabilis* displayed significant corrugation with collapsed and distorted cork cells. The lenticular channel in *Q. variabilis* virgin cork was surrounded by thick-walled cells filled with compact lenticular filling tissue surrounded by thick-walled cells (Prasetia *et al.* 2022a).

Regarding quantitative features, *Q. variabilis* virgin cork showed a smaller growth ring width and higher latecork percentage than *Q. suber* reproduction cork. In the transverse and radial D, Prasetia, B. D. Purusatama, J. H. Kim, J. H. Jang, S. Y. Park, and N. H. Kim

surfaces, *Q. variabilis* cork showed a lower frequency of pentagonal cork cells than *Q. suber* cork. On the tangential surface, *Q. variabilis* cork showed a lower frequency of heptagonal cells and a higher frequency of pentagonal cells than *Q. suber* cork. Cell width, lumen diameter, cell wall thickness, prism base edge and area, total cell volume, and solid cell wall volume in *Q. variabilis* virgin cork were smaller than those in *Q. suber* reproduction cork. The fractional solid volume and number of cells per cm³ in *Q. variabilis* virgin cork were higher compared to those in *Q. suber* reproduction cork (Prasetia *et al.* 2022b).

In conclusion, the qualitative and quantitative anatomical aspects of Q. variabilis virgin cork were distinctively different from Q. suber reproduction cork. Due to the structural characteristics of Q. variabilis virgin cork, applications require trituration to cork granules and agglomeration to produce cork composite products, while its cellular features allow considering it for insulation, surfacing, and sealant products. The results of this study may be used to evaluate the quality and identify Q. variabilis virgin cork grown in Korea for further utilization.

ACKNOWLEDGMENTS

This research was supported by the Science and Technology Support Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT) (NRF-2019K1A3A9A01000018, No. 2022R1A2C1006470), Basic Science Research Program through the NRF funded by the Ministry of Education (No. 2018R1A6A1A03025582), and R&D Program for Forest Science Technology (Project No. 2021350C10-2223-AC03) provided by the Korea Forest Service (Korea Forestry Promotion Institute).

REFERENCES

- H. Pereira, "Cork: Biology, Production, and Uses," Elsevier Publications: Amsterdam, the Netherlands, 2007
- [2] D. Prasetia, B. D. Purusatama, J. H. Kim, G. U. Yang, J. H. Jang, S. Y. Park, and N. H. Kim, "Qualitative anatomical characteristics of the virgin cork in *Quercus variabilis* grown in Korea," Bioresources, vol. 18, issue, 1, pp. 884-898, 2022a
- [3] D. Prasetia, B. D. Purusatama, J. H. Kim, G. U. Yang, J. H. Jang, S. Y. Park, and S. H. Lee, N. H. Kim, "Quantitative anatomical characteristics of virgin cork in *Quercus variabilis* grown in Korea," Forests, vol. 13, issue, 10, pp. 1711 2022b



MANUFACTURING OF CORK-STF COMPOSITES

G.J.A. Sousa*, R.J.A. de Sousa[†] and F.A.O. Fernandes[†]

* University of Aveiro Department of Mechanical Engineering Campus Santiago, 3810-193 Aveiro, Portugal e-mail: gui.sousa@ua.pt

[†] University of Aveiro Center for Mechanical Technology and Automation Campus Santiago, 3810-193 Aveiro, Portugal e-mail: <u>rsousa@ua.pt</u>

Keywords: Shear Thickening Fluids (STF), Cork Composites, Viscosity, Impact Strength

Abstract.

Shear thickening fluids (STF) viscosity significantly increases when subjected to an external dynamic load. Recent advances show their potential for engineering applications, such as the development of shock absorbers and impact energy-absorbing structures. There is a search for sustainable materials for several applications due to the critical need to replace nonrenewable raw materials. Cork is a sustainable material reported to be an excellent alternative to synthetic energy absorbers thanks to its cellular microstructure and cell-wall composition. This work focuses on the development of cork composites designed for impact energy mitigation and on their enhancement with STFs. The cork-STF composites were manufactured by compression molding, exploring different compositions of both raw materials. Additionally, the manufactured compounds were characterized by submitting samples to dynamic compression loading, particularly impacts. The results made it possible to conclude that for STF concentrations higher than 20%, deagglomeration occurs. On the other hand, good results were achieved with compounds that have less than 20% of STF in their composition, being able to withstand impact loading. Therefore, it was concluded that the impregnation of the cork compound with STF leads to a decrease in energy absorption. Nevertheless, the agglomeration was successful, and this design can be adapted for other specific purposes, applications or even strain rates than the ones explored in this work.

CHARACTERISTICS OF CORK PAVING MATERIALS MADE BY PROCESSED CORK GRANULES

Jae-Hyuk Jang1[†], Se-Kyung Sung1, Se-Yeong Park2 and Nam-Hun Kim2

 ¹ R&D Center, FC KOREA LAND Co., Ltd. Seoul 07271, Republic of Korea
 [†] Corresponding author e-mail: jhjang0503@gmail.com

² Dept. of Forest Biomaterials Engineering, College of Forest and Environmental Sciences, Kangwon National University Chuncheon 24341, Republic of Korea

Keywords: Cork granules, cork-based materials, paving materials, pavement

Abstract.

Cork granules are by-products after the production of various cork products, such as wine stoppers, and are considered a valuable resource because of their good elasticity and slip resistance. In the first study, the applicability of cork granules as paving materials for walkways and children's playgrounds was investigated. Cork granules with various particle sizes from 1 mm to 8 mm were obtained from Portuguese cork oak (Quercus suber). As a result of manufacturing cork paving materials with a thickness of 15 mm, their tensile strength was found to be 0.5 MPa or more. However, the tensile properties of the paving material made only with cork granules with a particle size smaller than 2 mm were less than 0.2 MPa. Furthermore, other physical properties of cork paving materials such as shock absorption, sliding resistance, and vertical deformation were all investigated as suitable for human activity. As a result of surface temperature measurement by a thermal imaging camera in summer, it was found that the cork paving material was more effective in alleviating the heat island phenomenon than the rubber one. In the second study, for the localization of cork resources, the cork granule manufacturing pattern from Quercus variabilis, which is known to have the thickest cork layer among domestic species in Korea, was evaluated, and the cork paving material manufacturing potential was evaluated. The 57-year-old oak (approximately 40 cm in diameter at breast height) collected from the academic forest of Kangwon National University is classified into details such as the

J.H. Jang, S.K. Sung, S.Y. Park and N.H. Kim

outer bark (including the cork layer), the inner bark, and the wood, and pulverize each of them in a cutter mill-type grinder for the same time. The shape and particle distribution of water were evaluated. As a result, the outer bark containing the cork layer showed an amorphous granular shape by pulverization, the inner bark was powdery, and the xylem was needle like shaped. About 1% of the total pulverized material of the outer bark was scattered and lost during pulverization and sampling, and about 31% had a particle size of 2 mm or less. About 68% of the total pulverized material was found to exceed 2 mm. Among them, the distribution of particles for installing the lower layer of cork paving material (more than 5 mm) was the highest, and the distribution of particles for installing the above-mentioned upper and lower layers were selected to manufacture cork paving materials for children's activity spaces, and their safety was evaluated by the HIC safety test method. As a result of the HIC safety inspection, the domestic oyster oak-based cork paving material did not show a significant difference from the case manufactured based on imported products, and it sufficiently exceeded the test standard of 1,000 or less even if the thickness of the finished product was varied.



Figure 1. Cross sectional view of cork paving materials.



Figure 2. Application cases of cork paving materials.

ACKNOWLEDGEMENT

This study was carried out with the support of 'R&D Program for Forest Science Technology (Project No. 2021350B10-2123-AC03)' provided by Korea Forest Service (Korea Forestry Promotion Institute)



CONTRIBUTION TO THE CHARACTERIZATION OF CORKS' USE-LIFE

Ana Lopes Cardoso*, Cristina L.M. Silva† and Fátima Poças †

* Cork Supply Portugal Rua Nova do Fial, 102, 4536-907 S. Paio Oleiros, Portugal e-mail: <u>acardoso@corksupply.pt</u>

[†] Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Portugal e-mail: <u>clsilva@ucp.pt</u> <u>fpocas@ucp.pt</u>

Keywords:

Abstract.

Oxygen permeability data is relevant for selecting wine bottle closures, but the impact of wine contact, temperature, and time use has not yet been explained. Market available stoppers were analysed for oxygen ingress over time in stoppered bottles, under different temperatures, with and without contact between the cork and wine simulant. The Weibull model described well the oxygen ingress. Differences were found between cork types, in long-term oxygen pressure values and ingress rates. The temperature effect followed an Arrhenius behaviour, with statistical significance only for micro agglomerated corks. Micro agglomerated corks exhibited slower initial oxygen ingress but higher long-term oxygen ingress than natural corks. Principal Component Analysis (PCA) showed that factors related to the bottleneck-cork interface contributed more to the variance of the system than the cork type. Liquid contact reduces oxygen ingress rate around five times. The temperature impact in the oxygen ingress was lower for natural corks than for micro agglomerated corks.

INTRODUCTION

Despite corks being used as a closure for bottled wine for a long time, they still lack confirmation for the reasons of their effectiveness and the changes in their performance during the use period.

Much of the research regarding cork performance has been conducted in the sense of bottled wine ageing [2], [16], [17]. Other research work has been conducted in the context of determining the permeability under different test conditions [9], [10] or analysing the applicable mass transfer models [1], [3], [8]. Reviews have been presented to describe the complexity of the wine bottles' closure system [5], [6].

The rationale of the current study considers that significant improvements in the reliability of closure performance can only be achieved by closer attention to the parameters that affect cork closure performance. The ongoing project aims to investigate the preservation of cork properties by analysing their mechanical behaviour; permeability to gases; wine-cork interactions, and fatigue analysis.

BACKGROUND

The research focuses on cork behaviour regarding mechanical properties and permeability to oxygen, considering both wine-cork interactions, bottleneck, and temperature.

Market available stoppers, natural and micro agglomerated (technical) corks, were analysed, under different temperatures (8, 23, and 40 °C), with and without contact between cork and wine simulant.

Compression pattern differs from natural to micro agglomerated corks. The compression behaviour has been reported with properties of flexible cellular materials exhibiting compression curves (stress-strain) with three regions [12]. Recovery tests aim at bringing insights into elastic properties decay and show different mechanical contours of natural and micro agglomerated corks.

The empirical Weibull model describing the oxygen ingress in the bottle over time (equation (1)) described well the observed data. This model has been used to describe various processes in food processing, quality, and safety, including the mass transfer of additives from plastics into food [14].

Differences were found between cork types in long-term oxygen pressure (Po) and ingress rates (τ). Micro agglomerated corks exhibited slower initial oxygen ingress but higher

Lopes Cardoso A., Silva C. L. M. and Poças F.

long-term oxygen ingress than natural corks. Liquid contact reduces oxygen ingress around five times. The temperature impact in the oxygen ingress was lower for natural corks. Principal Component Analysis (PCA) showed that factors related to the bottleneck-cork interface contributed more to the variance of the system than the cork type.

The data obtained for oxygen ingresses allows modelling the effect of temperature in the range of 8 to 40 °C for predicting the behaviour under varying conditions of storage or transportation.

FIGURES

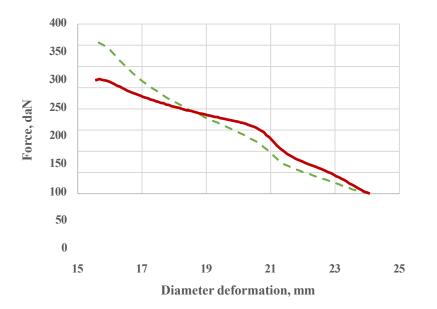
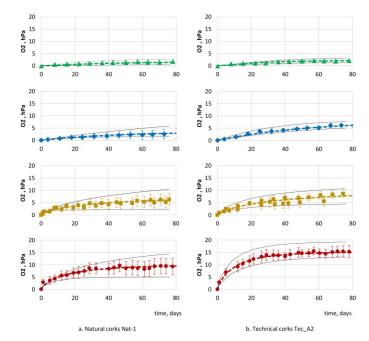


Figure 1. Compression profile of natural (-) and technical (-) corks



Lopes Cardoso A., Silva C. L. M. and Poças F.

Figure 2. Monitoring of oxygen ingress along time (dots for average, bars for standard deviation). Test with wine simulant contact at 23 °C (\blacktriangle); Test in dry condition at 8 °C (\blacklozenge), 23 °C (\blacksquare), 40 °C (\bullet). - - - - model fit. ----- upper and lower curves represent the replicates with the higher deviation from the average curve.

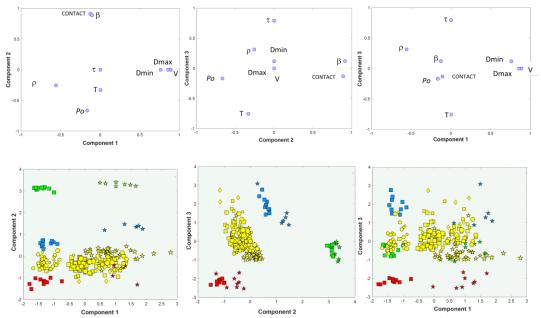


Figure 3: PCA loadings and score plots with all variables. Natural (\Rightarrow), Tec_A (\Box), Tec_C (\diamond). Symbol colour for temperatures: blue 8 °C, yellow 23 °C, red 40 °C and green for 23 °C under wet condition. Symbol sizes for different closures lengths

EQUATIONS

The Weibull model is an empirical model that considers two parameters τ and β .

$$p(t) = p \quad (\qquad t \quad) \tag{1}$$

Lopes Cørdoso A., Silva C. L. M. and Poças F.

$$1 - exp(--)$$

where p(t) is the oxygen partial pressure inside the bottle changing with time t, p_0 is the pressure at equilibrium, and the initial pressure is considered zero.

 τ is the system time constant associated with the process rate and has been found to depend on the temperature following an Arrhenius-type behaviour The parameter β and the corresponding shape of the curve at earlier times was found to relate to different mechanisms controlling the mass transfer.

REFERENCES

- Brazinha, C., Fonseca, A., Pereira, H., Teodoro, O., Crespo, J. (2013). Gas transport through cork: Modelling gas permeation based on the morphology of a natural polymer material. *Journal of Membrane Science*, 428, 52-62. doi:10.1016/j.memsci.2012.10.019
- [2] Chevalier, V., Pons, A., Loisel, C. (2019). Impact of stoppers on the aging of wine. Part 1 of 3 Characterization of oxygen transfer with cork stoppers. *REVUE DES ŒNOLOGUES*, 170. Retrieved from pict.oeno.tm.fr/documents/16501/2869401/x_TAP_web_Chevalier_170_partie1-3_Impact-de-lobturateur-sur-le-vieillis_En.pdf
- [3] Crouvisier-Urion, K., Bellat, J.-P., Gougeon, R. D., Karbowiak, T. (2018). Gas transfer through wine closures: A critical review. *Trends in Food Science Technology*, 78, 255-269. doi:10.1016/j.tifs.2018.05.021
- [4] Diéval, J.-B., Vidal, S., Aagaard, O. (2011). Measurement of the Oxygen Transmission Rate of Coextruded Wine Bottle Closures Using a Luminescence-Based Technique. *Package. Technol. Sci., 24*, 375-385. doi:10.1002/pts.945
- [5] Karbowiak, T., Crouvisier-Urion, K., Lagorce, A., Ballester, J., Geoffroy, A. (2019). Wine aging: a bottleneck story. *Science of Food*, 3(1), 14. doi:10.1038/s41538-019-0045-9
- [6] Karbowiak, T., Gougeon, R., Alinc, J.-B., Brachais, L., Debeaufort, F., Voilley, A., Chassagne, D. (2010). Wine Oxidation and the Role of Cork. *Critical Reviews in Food Science and Nutrition*, 50(1), 20 52. doi:10.1080/10408390802248585
- [7] Lagorce-Tachon, A., Karbowiak, T., Paulin, C., Simon, J.-M., Gougeon, R. G., Bellat, J.-P. (2016).
 About the Role of the Bottleneck/Cork Interface on Oxygen Transfer. *Journal of Agricultural and Food Chemistry*, 64(35), 6672-6675. doi:10.1021/acs.jafc.6b02465
- [8] Lagorce-Tachon, A., Karbowiak, T., Simon, J.-M., Gougeon, R., Bellat, J.-P. (2014). Diffusion of

Lopes Cardoso A., Silva C. L. M. and Poças F. Oxygen through Cork Stopper: Is It a Knudsen or a Fickian Mechanism? *Journal of agricultural and food chemistry*, *62*, 9180. doi:10.1021/jf501918n

- [9] Lopes, P., Saucier, C., Teissedre, P.-L., Glories, Y. (2006). Impact of Storage Position on Oxygen Ingress through Different Closures into Wine Bottles. *Agric. Food Chem.*, 54(18), 6741-6746. doi:10.1021/jf0614239
- [10] Lopes, P., Saucier, C., Teissedre, P.-L., Glories, Y. (2007). Main Routes of Oxygen Ingress through Different Closures into Wine Bottles. J. Agric. Food Chem., 55(13), 5167-5170. doi:10.1021/jf0706023
- [11] Oliveira, V., Lopes, P., Cabral, M., Pereira, H. (2013). Kinetics of Oxygen Ingress into Wine Bottles Closed with Natural Cork Stoppers of Different Qualities. *American Journal of Enology* and Viticulture, 64, 395-399. doi:10.5344/ajev.2013.13009
- [12] Pereira, H. (2015). The Rationale behind Cork Properties: A Review of Structure and Chemistry. *BioResources*, 10(3), 6207-6229. doi:10.15376/BIORES.10.3.PEREIRA
- [13] Poças, M. F., Ferreira, B., Pereira, J., Hogg, T. (2010). Measurement of Oxygen Transmission Rate through Foamed Materials for Bottle Closures. *Package. Technol. Sci.*, 23, 27-33. doi:10.1002/pts.876
- [14] Poças, M. F., Oliveira, J. C., Brandsch, R., Hogg, T. (2012). Analysis of Mathematical Models to Decribe the Migration of Additives from Packaging Plastics to Foods. *Journal of Food Process Engineering*, 35(4), 657-676. doi:10.1111/j.1745-4530.2010.00612.x
- [15] Rosa, M. E. and Fortes, M. A. (1988). Rate effects on the compression and recovery of dimensions of cork. J. Mater. Sci., vol. 23, no. 3, pp. 879–885. doi.org/10.1007/BF01153983
- [16] Vidal, J.-C., Moutounet, M. (2011). Impact des conditions operatoires au conditionnement et de la permeabilite du bouchon sur l'oxygene et l'evolution d'un vin blanc de sauvignon en bouteille. retrieved from Revue Internet de Viticulture et œnologie: researchgate.net/publication/341773277_Impact_des_conditions_operatoires_au_conditionne ment_et_de_la_permeabilite_du_bouchon_sur_l'oxygene_et_l'evolution_d'un_vin_blanc_de_s auvignon_en_bouteille
- [17] Vidal, J.-C., Caillé, S., Samson, A., Salmon, J.-M. (2017). Comparison of the effect of 8 closures in controlled industrial conditions on the shelf life of a red wine. *BIO Web of Conferences 9*. doi:10.1051/bioconf/20170902024



CORK USES IN ARCHITECTURE: BENEFITS FOR NZEB

Verissimo, Cristina

Dalhousie University Faculty of Architecture and Planning PO Box 15000 5410 Spring Garden Road Halifax, Nova Scotia, Canada, B3H 4R2 e-mail: cverissimo@dal.ca Keywords: Cork, sustainable materials, NZEB, Architecture, culture

Abstract.

There is an increase interest of the use of cork in architecture, due to the diversity and quality of products offered by the industry and its sustainable energy value. Cork can contribute to the NZEB concept from the point of view of the architecture. Its energy performance as a diverse construction material, can contribute to an energy-efficient and sustainable building.

It is relevant to assess the various possibilities in which this material can contribute to the NZEB concept. Namely cork as a construction material, as energy performance of buildings, helping to make them fit into this normative class, contributing to an energy-efficient and sustainable building, and exploring future opportunities for the evolution of this concept and its contribution from architecture.

INTRODUCTION

Cork is a natural, recyclable, renewable and non-toxic resource, with strong impact in Mediterranean culture and ecosystems for centuries. Cork is very versatile and adopts different technological transformation processes, giving rise to several products, which can be used in different applications. Cork products for the construction industry are most suitable for sustainable and efficient energy construction, given its mentioned ecological characteristics. In addition, these products contribute to general comfort and indoor air quality [1].

Nearly zero-emission building (NZEB) means a building that has a very high energy performance, while the nearly zero or very low amount of energy required should be covered to a very significant extent by energy from renewable sources, including energy from renewable sources produced on-site or nearby [2]. The Energy Performance of Buildings Directive requires that EU countries had to ensure that all new buildings were nearly zero- energy by the end of 2020 while all new public buildings had to be nearly zero-energy. The Commission's proposal to revise the directive (December 2021) makes a step forward from current NZEB to zero-emission building (ZEB), aligning the energy performance requirement for new buildings to the longer-term climate neutrality goal and "energy efficiency first principle" [2].

According to the directive's proposal, a zero-emission building is as a building with a very high energy performance, with the very low amount of energy still required fully covered by energy from renewable sources and without on-site carbon emissions from fossil fuels. This will be applied to all new buildings by 1 January 2027, and to all new buildings occupied or owned by public authorities. [3].

This European Directive Proposal brought new demands for architects when they design buildings. Especially the materials selection criteria imply less fossil fuel energy materials and more natural and ecologic materials such as cork products.

CORK IMPORTANCE IN ARCHITECTURE

Cork is very versatile and adopts different technological transformation processes, giving rise to several products, which can be used in different applications. New demands for cork give rise to new technologies that can replace traditional methods of boiling the cork, through a microwave process that maintains cork qualities but expands the material's capacity to three times more than its original size. Meanwhile, cork products for the construction industry are most suitable and efficient energy construction, given its mentioned ecological characteristics. In addition, these products contribute to general comfort and indoor air quality (Gil, 2007). This gives an opportunity in architecture for the use of cork as a primary material as in the past. In the last decade some examples of the use of cork have emerged, such as: Portugal Pavilion for Expo 2000 Hannover exhibition, Serpentine Pavilion, London, 2012, Logowines Winery / PMC Arquitectos. Cork House in Berkshire, England.

The various cork products for civil construction can make a significant contribution to making them fit into the NZEB normative class, contributing to an energy-efficient and sustainable building. Cork materials allows to reduce the energy needs in construction [4]. Cork is a carbon sequestration material with good benefits of thermal comfort when applied to: insulation, facades, or even flooring. Examples of these applications show the long-term benefits in the use of cork.

REFERENCES

- L. Gil, "Cork as a building material. Technical manual". Santa Maria de Lamas: Apcor. 2007
- [2] An official website of the European Union: "Nearly zero-energy buildings". Available from: <u>https://energy.ec.europa.eu/topics/energy-efficiency/energy-efficientbuildings/nearly-zero-energy-</u> <u>buildings_en#:~:text=Nearly%20zero%2Demission%20building%20(NZEB,produced%2</u> 0on%2Dsite%20or%20nearby. [accessed Feb. 2023].
- [3] An official website of the European Union: European Green Deal: "Commission proposes to boost renovation and decarbonisation of buildings" <u>https://ec.europa.eu/commission/presscorner/detail/en/ip_21_6683</u>, 15 December 2021

[4] L. Gil, A cortiça e o conceito NZEB. Available from: https://www.researchgate.net/publication/360561578_A_cortica_e_o_conceito_NZEB [accessed Feb. 2023].

MAGNESIUM-MODIFIED CORK BIOCHARS FOR THE REMOVAL OF PHOSPHATE FROM WATER

Ariana M.A. Pintor^{*†}, Nuno F. R. Sousa^{*†}, O. Salomé G.P. Soares^{*†}, M. Fernando R. Pereira^{*†} and Cidália M.S. Botelho^{*†}

 * LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and

Materials

Faculty of Engineering, University of Porto
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[†] ALiCE - Associate Laboratory in Chemical Engineering
Faculty of Engineering, University of Porto
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
e-mail: ampintor@fe.up.pt (Ariana M.A. Pintor)

Keywords: Biochar, phosphorus, cork, magnesium

Phosphorus is an essential nutrient for life, namely the growth of plants, and is, therefore, widely used in the fertilisation of crops. Conventional fertilisers are usually extracted from phosphate rock, a finite, non-renewable resource predicted to be exhausted in the next 50 to 100 years [1]. For this reason, better phosphorus management, given a circular economy, is being sought. At the same time, phosphorus leaching into water bodies through wastewater disposal or agricultural runoff causes eutrophication, a grave environmental problem that endangers the health of aquatic life [2]. For this reason, the sequestration of excess phosphorus from water and wastewater is increasingly regarded as an alternative path for recycling this nutrient.

Biochar is a black carbon material produced by pyrolysis of lignocellulosic biomass in the absence of oxygen. It presents numerous advantages as a soil amendment, leading to the sequestration of carbon, which contributes to climate change mitigation [3]. Cork, the bark of *Quercus suber* L., is a good candidate for biochar production, given its unique cellular structure and chemical composition [4].

Biochar can be engineered to improve its contents in certain components and enhance its adsorption capacity, promoted by the larger surface area than its precursors [5]. In this study, we have produced magnesium-modified biochars using cork granulates to uptake phosphorus from water. Cork granulates were transformed into magnesium-modified biochars by chemical

Ariana M.A. Pintor, Nuno F.R. Sousa, O. Salomé G.P. Soares, M. Fernando R. Pereira and Cidália M.S. Botelho modification and thermal treatment. The materials were found to have an excellent uptake capacity for phosphorus compared to similar biochars previously reported.

The carbon materials enriched with magnesium and phosphorus can further be applied as fertilisers in the soil since both magnesium and phosphorus are essential to plants' growth [6]. Through this process, the recycling of phosphorus from water and wastewater flows is achieved while at the same time providing added value to a byproduct of the cork industry.

ACKNOWLEDGMENTS

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC). A. Pintor acknowledges her Junior Researcher contract [CEECIND/01485/2017] by FCT.

REFERENCES

- D.P. Van Vuuren, A.F. Bouwman, and A.H.W. Beusen, "Phosphorus demand for the 1970-2100 period: A scenario analysis of resource depletion", Global Environ. Change, vol. 20, no. 3, pp. 428-439, 2010.
- [2] C.P. Mainstone, and W. Parr, "Phosphorus in rivers ecology and management", Sci. Tot. Environ., vol. 282-283, pp. 25-47, 2002.
- [3] D. Mohan, A. Sarswat, Y.S. Ok, and C.U. Pittman Jr., "Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review", Biores. Technol., vol. 160, pp. 191-202, 2014.
- [4] Q. Wang, Z. Lai, J. Mu, D. Chu, and X. Zang, "Converting industrial waste cork to biochar as Cu(II) adsorbent via slow pyrolysis", Waste Manag., vol. 105, pp. 102-109, 2020.
- [5] I. W. Almanassra, G. Mckay, V. Kochkodan, M.A. Atieh, and T. Al-Ansari, "A state of the art review on phosphate removal from water by biochars", Chem. Eng. J., vol. 409, no. 128211, 2021.
- [6] H. Bacelo, A.M.A. Pintor, S.C.R. Santos, R.A.R. Boaventura, C.M.S. Botelho, "Performance and prospects of different adsorbents for phosphorus uptake and recovery from water", Chem. Eng. J., vol. 381, no. 122566, 2020.

NEW HYBRID STRUCTURES BASED ON ALUMINIUM FOAMS AND CORK GRANULES

Isabel Duarte*, Susana C. Pinto*, Paula A.A.P. Marques*

M. Vesenjak[‡],V.H. Carneiro[†], Lovre Krstulović-Opara[†]

* University of Aveiro Department of Mechanical Engineering TEMA-Center for Mechanical Technology and Automation LASI - Intelligent Systems Associate Laboratory, Portugal Campus Santiago, 3810-193 Aveiro, Portugal Corresponding author: isabel.duarte@ua.pt ‡ University of Maribor

Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia;

[†] University of Minho Department of Mechanical Engineering MEtRICs Campus de Azurém, 4800-058 Guimarães, Portugal

University of Split Faculty of Electrical Eng., Mechanical Eng. and Naval Architecture R. Boskovica 32, 21 000 Split, Croatia

Keywords: Cellular materials, hybrid structures, cork, open-cell aluminium foam

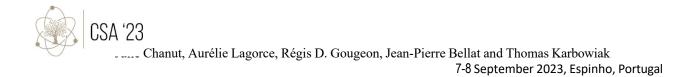
Abstract. Hybrid structures based on open-cell aluminium foam [1-2] have been developed to obtain cellular structures with high structural efficiency and a large capacity to absorb impact energy, while damping noise and vibration. The present paper focuses on the fabrication and characterization of new hybrid structures prepared by combining open-cell aluminium foam and cork granules. Additionally, the impact of reinforcing cork granules with graphene-based materials was also detailed. A new fabrication methodology was developed and patented [3] in which these aluminium foam-cork hybrid structures are prepared by filling the cellular pores of the aluminium foam with cork granules (unreinforced or reinforced with carbon nanostructures). These resulting hybrid structures are lightweight, multi-functional, recyclable and non-flammable, ideal for sustainable and environmentally friendly design. Results have

Isabel Duarte, Susana C. Pinto, Paula A.A.P. Marques, M. Vesenjak, V. Carneiro, and Lovre Krstulović-Opara shown that the new aluminium foam-cork hybrid structures have excellent sound-absorbing properties combined with efficient strength-to-weight and stiffness-to-weight ratios. It is also shown that adding reinforcing the cork granulates with graphene-based materials improves sound-absorbing properties and enhances the fire-resistant characteristic.

Acknowledgment. This research has been supported by the UIDB/00481/2020 and UIDP/00481/2020 (FCT); and CENTRO-01-0145-FEDER-022083, Centro2020, under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund.

REFERENCES

- I. Duarte, M. Vesenjak, L. Krstulović-Opara, Z. Ren, "Crush performance of multifunctional hybrid foams based on an aluminium alloy open-cell foam skeleton", Polymer Testing, vol. 67, pp. 246-256, 2018.
- [2] S.C. Pinto, P.A.A.P. Marques, M. Vesenjak, R. Vicente, L. Godinho, L. Krstulović-Opara,
 I. Duarte, "Characterization and physical properties of aluminium foam– polydimethylsiloxane nanocomposite hybrid structures", Composite Structures, vol. 230, 111521, 2019.
- [3] I. Duarte, S. C. Pinto, P.A.A.P. Marques. "Metais e estruturas metálicas porosos e celulares de porosidade aberta impregnados com cortiça, seus processos de produção e suas utilizações" Patente de invenção n.º 2021070155. Despacho de concessão de 2022.12.20.



OXYGEN TRANSFER: THE CRUCIAL ROLE OF THE GLASS-CORK INTERFACE

Julie Chanut*, *, Aurélie Lagorce*, Régis D. Gougeon†, Jean-Pierre Bellat* and Thomas Karbowiak*

* Univ. Bourgogne Franche-Comté, Institut Agro Dijon, PAM UMR 02 102, 1 Esplanade Erasme, 21000 Dijon, France e-mail: thomas.karbowiak@agrosupdijon.fr

^{*} Univ. Bourgogne Franche-Comté, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS, 9 Avenue Alain Savary, 21000 Dijon, France

[†] Univ. Bourgogne Franche-Comté, Institut Universitaire de la Vigne et du Vin, 1 rue Claude Ladrey, 21000 Dijon, France

Keywords: Wine oxidation, Cork / Bottleneck Interface, Oxygen transfer, Surface treatment

Abstract.

During wine conservation in bottle, the control of oxygen transfer from the outside environment to the wine inside the bottle is a key parameter that determines the wine quality. Obviously, many other factors can also influence the evolution of wine during postbottling aging, such as the composition of the wine itself, the temperature, the relative humidity, the storage position, as well as the amount of oxygen initially present in the bottle [1-3]. However, the oxygen transfer is the most critical factor. For this reason, the choice of the packaging and in particular of the stopper is crucial in providing the best conditions for wine aging. For the various types of corkbased stoppers currently used, an additional outer layer of a surface treatment product is always applied in the final step of the manufacturing process. The primary function of these surface treatments is to facilitate the introduction and the extraction of the stopper from the bottleneck, as they reduce the adhesion between the glass and the cork, acting as a slippery agent. However, only a few studies have reported the effect of such coating agents on the transfer of oxygen through the cork-bottleneck system [4].

A comprehensive study was carried out on microagglomerated cork stoppers to investigate the role played by the interface between the stopper and the bottleneck on the oxygen ingress into the bottle, as well as the effect of the surface treatment of the stopper. This was performed starting from the diffusion through the stopper alone and ending with a more complex system

Julie Chanut, Aurélie Lagorce, Régis D. Gougeon, Jean-Pierre Bellat and Thomas Karbowiak comprising the stopper covered by a surface treatment agent and compressed in the glass bottleneck [5-7]. First, the compression of cork, at a value close to 40% (V/V), corresponding to still wines, had a limited effect on the oxygen transfer, with only a slight decrease of the oxygen diffusion. Second, once the cork, without any surface treatment, was inserted into the glass bottleneck, up to 99% of the total oxygen transfer occurred at the stopper / bottleneck interface. Third, when the cork surface was coated with a paraffin-silicone mixture, there was almost no oxygen transfer at the interface. Therefore, in addition to its initial role of ensuring easier uncorking, the surface coating confers an additional and unexpected barrier efficiency to the wine sealing system

REFERENCES

 [1] T. Karbowiak, R. D. Gougeon, J.-B. Alinc, L. Brachais, F. Debeaufort, A. Voilley and D. Chassagne, Wine oxidation and the role of cork. Crit. Rev. Food Sci. 50 (2010) 20-52. <u>https://doi.org/10.1080/10408390802248585</u>

[2] P. Lopes, M. A. Silva, A. Pons, T. Tominaga, V. Lavigne, C. Saucier, P. Darriet, M. Cabral, P.-L. Teissedre and D. Dubourdieu, Impact of the Oxygen Exposure during Bottling and Oxygen Barrier Properties of Different Closures on Wine Quality during Post-Bottling, in: Flavor Chemistry of Wine and Other Alcoholic Beverages, 2012, pp. 167-187

[3] F. Venturi, C. Sanmartin, I. Taglieri, Y. Xiaoguo, G. Andrich and A. Zinnai, The influence of packaging on the sensorial evolution of white wine as a function of the operating conditions adopted during storage. Agrochimica 60 (2016) 150-159. <u>https://doi.org/10.12871/0021857201627</u>

[4] C. P. Keenan, M. Y. Gozukara, G. B. Y. Christie and D. N. Heyes, Oxygen permeability of macrocrystalline paraffin wax and relevance to wax coatings on natural corks used as wine bottle closures. Aust. J. Grape Wine R. 5 (1999) 66-70. <u>https://doi.org/10.1111/j.1755-0238.1999.tb00154.x</u>

[5] J. Chanut, J.-P. Bellat, R. D. Gougeon and T. Karbowiak, Controlled Diffusion by Thin Layer Coating: The Intricate Case of the Glass-Stopper Interface. Food Control 120 (2021) 107446. <u>https://doi.org/10.1016/j.foodcont.2020.107446</u>

[6] J. Chanut, A. Lagorce, S. Lequin, R. D. Gougeon, J.-M. Simon, J.-P. Bellat and T. Karbowiak, Fast manometric method for determining the effective oxygen diffusion coefficient through wine stopper. Polymer Testing 93 (2021) 106924. https://doi.org/10.1016/j.polymertesting.2020.106924

[7] A. Lagorce-Tachon, T. Karbowiak, C. Paulin, J.-M. Simon, R. D. Gougeon and J.-P. Bellat, About the Role of the Bottleneck/Cork Interface on Oxygen Transfer. J. Agri. Food Chem. 64 Julie Chanut, Aurélie Lagorce, Régis D. Gougeon, Jean-Pierre Bellat and Thomas Karbowiak (2016) 6672-6675. <u>https://doi.org/10.1021/acs.jafc.6b02465</u>



INDUSTRIAL METHOD FOR NON-DESTRUCTIVELY SCREENING WINE CORK STOPPERS FOR 2,4,6-TRICHLOROANISOLE BELOW THE PERCEPTION THRESHOLD IN 2 SECONDS

Luca Cappellin*, Luigi Ciotti† and Manuel Andreas Hutterli†

* Dipartimento di Scienze Chimiche Università degli Studi di Padova 35131 Padova, Italy e-mail: <u>luca.cappellin@unipd.it</u>

[†] Tofwerk AG Schorenstrasse, 39 CH-3645 Thun, Switzerland e-mail: <u>luigi.ciotti@tofwerk.com; hutterli@tofwerk.com</u>

Keywords: Cork, trichloroanisole, mass spectrometry

Abstract.

2,4,6-trichloroanisole (TCA) contamination of wine causes huge economic losses for the wine industry estimated to amount at several billion dollars yearly. Over fifty years of studies have determined that this problem is often caused by TCA contamination of the cork stopper which releases TCA into the wine. The human sensory threshold for TCA is extremely low. A wine contaminated by 1-2 ng/L TCA can be perceived as tainted. Contaminations with <0.5 ng/L TCA are commonly considered negligible and are not perceivable. Quantitative TCA screening of individual cork stoppers during production would solve the problem. However, the vastly used traditional analytical methods have so far struggled to provide a fast and reliable enough industrial solution, whereas sensory analysis by trained panelists is time consuming and less quantitative. Here we propose a novel approach [1] based on chemical ionization - time of flight (CI-TOF) mass spectrometry employing the 'Vocus' ion source and ion-molecule reactor [2]. The technique proved capable of non-destructively quantifying TCA contamination in a single cork stopper in 2 s with a limit of quantification of 0.1 ng/L, well below the perception



threshold. A real test on industrial scale, quantifying TCA contamination in more than 1 million cork stoppers in about one month is shown, representing the largest dataset of TCA analysis on cork stoppers within the literature and proving the effectiveness of the technique in an industrial environment. The possibility to simultaneously quantify other off- flavors is also reported. Finally, the correlation with standard methods for releasable TCA quantification is discussed.

REFERENCES

[1] Cappellin, L. *et al.*; Analytical Chemistry 2020, 92 (14), 9823–9829. https://doi.org/10.1021/acs.analchem.0c01326

[2] Krechmer, J. *et al.*; Analytical Chemistry 2018, 90 (20), 12011–12018. <u>https://doi.org/10.1021/acs.analchem.8b02641</u>



LIQUID CRYSTALLINE SYSTEMS FROM CORK

1,4

Pedro Gil1, Ana P. C. Almeida^{1,2,3*}, Pedro L. Almeida and Maria Helena Godinho¹

1 i3N/CENIMAT, Department of Materials, NOVA School of Science and Technology Lisbon,

Portugal

2 LAQV/Requimte, Department of Chemistry, NOVA School of Science and Technology,

Caparica, Portugal

3 iBET Instituto de Biologia Experimental e Tecnológica, Oeiras, Portugal

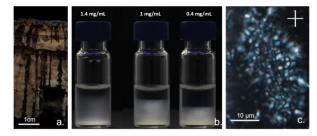
Lisbon's Superior Institute of Engineering, Polytechnic Institute of Lisbon, Lisbon, Portugal
 *email : ana.almeida@fct.unl.pt

Keywords: Composite materials, Liquid Crystals, Cellulose, Suberin

Portugal is the largest producer of cork from the *Quercus suber* (Figure a.). Major cork components include suberin (39-45%) and lignin (20%), while cellulose represents only 10-12% of its constituents [1, 2]. This work presents the study of liquid crystalline suspensions obtained from cellulose nanorods isolated from cork and the liquid crystalline phase obtained from suberin. The CNC suspensions exhibit an isotropic-birefringent phase separation over a wide range of particle concentrations (see figure b., diameter of the vials 1 cm). Furthermore, by polarizing optical microscopy (POM) between cross polarizers, characteristic liquid crystalline textures were identified, as shown (figure c.). In addition, solid films isolated from the initial and treated samples were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results are consistent with the self-assembly of the micro rods, isolated from cork, into a mesomorphic

cholesteric structure.

Figure 1 a. cork sample, b, vials presenting an isotropic upper phase and a birefringent high-density phase, c. polygonal fields texture observed between cross polars.



Acknowledgments

The authors acknowledged by the Associate Laboratory for Green Chemistry—LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020) and FCT-Fundação para a Ciência e a Tecnologia, I.P., in the scope of the projects



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

LA/P/0037/2020, UIDP/50025/2020 and UIDB/50025/2020 of the Associate Laboratory Institute of Nanostructures, Nanomodelling and Nanofabrication-i3N. A. Almeida is grateful for the financial support from Fundação para a Ciência e a Tecnologia, Portugal, through project 2022.01619.PTDC.

REFERENCES

- [1] A.V. Marques, H. Pereira, ANAIS ISA, 42,321 (1987).
- [2] M.A. Fortes, COLÓQUIO CIÊNCIA, 35 (1990).
- [1] Y. Habibi, L. A. Lucia, O. J. Rojas, CHEM. REV., 110(6), 3479-3500 (2010).



MAGNETIC CORK-DERIVED POROUS COMPOSITES AS ADSORBENTS FOR WATER REMEDIATION TECHNOLOGIES

Giovanna G. S. Grous*, Paulo Macedo† and Carlos M. Granadeiro*

* LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

e-mail: gisantos143@gmail.com; cgranadeiro@fc.up.pt

[†]J. A. Veiga de Macedo S.A., 4536-904, Santa Maria de Lamas, Portugal

Keywords: Cork composites, Biomass valorization, Superparamagnetism, Adsorption, Antibiotics.

Abstract. Cork, a renewable lignocellulosic material, is obtained from the bark of cork oak and its sustainable harvesting promotes regeneration without interfering in soil enrichment or carbon sequestration.[1] Cork industry generates a considerable amount of cork waste from the cork stopper manufacturing process, which is typically burned as source of energy.[2]. Recently, there has been an increasing interest in the preparation of waste-derived materials as alternative adsorbents due to its low cost, sustainability, wide availability of feedstocks and remarkable adsorptive capacities.[3]

We have explored the potential application of cork powder (CP) in the preparation of advanced magnetic adsorbents with enhanced adsorptive capabilities for water remediation. CP was used to produce two types of composite materials following different synthetic methodologies. The first method involves the impregnation of previously synthesized magnetite nanoparticles (MNP) into the porous framework of cork powder (MNP_CP), while the second involves the impregnation of CP with a selected transition metal (Fe) followed by pyrolysis under inert atmosphere, leading to the formation of a magnetic biochar (Fe_BCP). The adsorptive ability of the magnetic cork-derived materials was evaluated for the removal of fluoroquinolone antibiotics, using levofloxacin as model molecule. The adsorption studies were carried out by fluorescence spectroscopy through monitoring of the fluorescent emission of levofloxacin. Optimization of the experimental parameters, namely initial pH, contact time, adsorbent loading, was performed and adsorptive capacities in short periods of time for the removal



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

of levofloxacin from aqueous solutions. The proposed materials combine the low cost of the precursors, sustainable transformation of solid wastes into value-added products, easy magnetic separation and adsorptive performance highlighting its exceptional potential for application in water remediation.

REFERENCES

- [1] A. Matos, et al., Mater. Des., vol. 85, pp.230-239, 2015.
- [2] H.-K. Lai, et al., Chem. Eng. J., vol. 332, pp. 717-726, 2018.
- [3] C.P. Silva et al., Bioresour. Technol., vol. 250, pp. 888-901, 2018.

Ana Filipa L.O.M. Santos, António C. S. Ferreira

TCA SMART SENSOR FOR PROCESS CONTROL IN INDUSTRIAL SETTINGS

Ana Filipa L.O.M. Santos^{*}, António C. S. Ferreira[†]

^{*} Cork Supply Portugal, S.A. Rua Nova do Fial, 102, 4535-465 São Paio de Oleiros, Portugal e-mail: <u>fsantos@corksupply.pt</u>

[†]Cork Supply Portugal, S.A. Rua Nova do Fial, 102, 4535-465 São Paio de Oleiros, Portugal e-mail: <u>aferreira@corksupply.pt</u>

Keywords: TCA, cork, smart sensors; process control

INTRODUCTION

Cork taint in wine, described as "moldy-musty" aroma is commonly related to the chloroanisole family of compounds. 2,4,6-Trichloroanisole (TCA) is considered the major contributor to the sensory deviations related to cork due to its particularly low sensory threshold [1-3].

Methods for TCA analysis used, nowadays, in quality control (ISO 20752:2014 (E) [4] and OIV-MA-AS315-16 [5]) are very time consuming, destructive, and also incomplete since a limited number of samples per lot are analysed. To guarantee 100 % TCA taint free corks, Cork Supply developed in the past an industrial solution for TCA real time and non-destructive individual inspection, the DS100+ [6].

TCA is present along all the productive process, since forest to final cork, and the earlier it is detected in the process and segregated, the lower is its incidence on the final product.

In order to monitor this critical parameter, we develop a new system, a Smart Sensor a key element of Cork Supply Digital Transformation. This new process control unit is a component of a larger end-to-end (E2E) platform aiming to collect data from a sensor, processes it, and distributes information enabling, traceability and data-driven decision making to quality

Ana Filipa L.O.M. Santos, António C. S. Ferreira

aspects. Furthermore, making use of machine learning eliminates the need of qualified personnel to acquire and process data.

The Smart Sensor is capable to monitor TCA at different steps of cork manufacturing throughout the value chain, not requiring a trained analyst, compatible with industrial environments, smart, autonomous and reliable.

In this work we aim to present the results we collect from forest to final cork with our new industrial system and show the performance of this kind of devices towards the analysis of different cork materials.

REFERENCES

- R. F. Simpson, M. A. Sefton, "Origin and fate of 2,4,6-trichloroanisole in cork bark and wine corks," Aust. J. Grape Wine Res., vol 13, pp 106-116, 2007.
- [2] S. Boutou, P. Chatonnet, "Rapid headspace solid-phase microextraction/gas chromatographic/mass spectrometric assay for the quantitative determination of some of the main odorants causing off-flavours in wine," J. Chromatogr. A, vol 1141, pp 1-9, 2007.
- [3] C. S. S. Teixeira, A. C. S. Ferreira, N. M. F. S. A. Cerqueira, "Studying haloanisoles interaction with olfactory receptors," ACS Chem. Neurosci., vol. 7, pp 870-885, 2016.
- [4] ISO Cork Stoppers Determination of Releasable 2,4,6-Trichloroanisole (TCA).
 ISO20752:2014 (E), 2014.
- [5] OIV Detremination of Releasable 2,4,6-Trichloroanisole in wine by Cork Stoppers (Resolution OIV-Oeno 296/2009). Method OIV-MA-AS315-16 2001.
- [6] A. C. S. Ferreira, A. C. A. L. Cardoso, "Method for detecting a volatile analyte for classing and sorting cork stoppers depending on the concentration of the analyte," 2015, EP 3 165 918 A10.



NEW INSIGHTS ON THE MECHANICAL PROPERTIES OF CORK IN COMPRESSION

M. Gerometta*[†], X. Gabrion[†], A. Lagorce^{*}, S. Thibaud[†] and T. Karbowiak^{*}

 * Univ. Bourgogne Franche-Comté, Institut Agro Dijon UMR PAM A 02.102
 1 Esplanade Erasme, 21000 Dijon, France e-mail: thomas.karbowiak@agrosupdijon.fr

[†] SUPMICROTECH, CNRS, Institut FEMTO-ST, F-25000 Besançon,

Keywords: cork, structure, quasi-static compression test, repeated loading test, DIC

Abstract

Cork is a lightweight natural material with good chemical stability, low liquid permeability, a fairly high gas barrier and thermal-acoustic insulation properties [1]. It also has remarkable mechanical behaviour, especially in compression, enabling it to undergo large deformations of up to 80 % strain [2, 3]. All these properties have led to the use of cork for various material engineering applications, but its main use obviously remains the manufacturing of cork stoppers for wine. Due to its specific alveolar structure, cork displays a mechanical behaviour typical of a cellular material.

Despite the fact that the mechanical behaviour of cork has already been described in many works related to its properties in compression [4, 5, 6], some fundamental aspects still need to be clarified. Firstly, the relationship between the structure and the mechanical behaviour in compression, as evidenced by the stress-strain curve, requires a better understanding. Secondly, the interpretation of the elastic modulus and, in particular, the contribution of lenticels and phellem to the stiffness of the material still have to be investigated. To that purpose two methods were applied: a quasi-static test and a repeated loading test in compression. The elastic modulus

M. Gerometta, X. Gabrion, A. Lagorce, S. Thibaud, and T. Karbowiak was also determined using different devices: the crosshead, the extensioneter and the digital image correlation.

REFERENCES

- [1] Pereira, H. (2007). Cork: biology, production and uses. Amsterdam, Elsevier Science B.V.
- [2] Lagorce-Tachon, A., T. Karbowiak, D. Champion, R. D. Gougeon and J.-P. Bellat (2015)."Mechanical properties of cork: effect of hydration." Materials & Design 82: 148-154.
- [3] Lagorce-Tachon, A., T. Karbowiak, D. Champion, R. D. Gougeon and J.-P. Bellat (2016).
 "How does hydration affect the mechanical properties of wine stoppers?" Journal of Materials Science 51(9): 4227-4237.
- [3] Anjos, O., H. Pereira And M. E. Rosa (2008). "Effect of quality, porosity and density on the compression properties of cork." Holz Als Roh- Und Werkstoff 66(4): 295-301.
- [4] Oliveira, V., M. E. Rosa And H. Pereira (2014). "Variability of the compression properties of cork." Wood Science And Technology 48(5): 937-948.
- [5] Giunchi, A., A. Versari, G. P. Parpinello and S. Galassi (2008). "Analysis of mechanical properties of cork stoppers and synthetic closures used for wine bottling." Journal of Food Engineering 88(4): 576-580.
- [6] Crouvisier-Urion, K., J.-P. Bellat, R. D. Gougeon and T. Karbowiak (2018). "Mechanical properties of agglomerated cork stoppers for sparkling wines: Influence of adhesive and cork particle size." Composite Structures 203: 789-796.



IMPACT OF BOTTLENECK SHAPE ON CORK STOPPERS FUNCTIONAL PARAMETERS

André R. H. Pereira^{†*}, Sofia A. Matos^{*}, José P. S. Aniceto[†], Ana Lopes Cardoso^{*}

* Cork Supply Portugal Rua Nova do Fial, 102, 4536-907 S. Paio Oleiros, Portugal e-mail: <u>smatos@corksupply.pt</u> acardoso@corksupply.pt

> [†] University of Aveiro Campus Santiago, 3810-193 Aveiro, Portugal e-mail: <u>andrerosahp@ua.pt</u> joseaniceto@ua.pt

Keywords: Cork stoppers, bottleneck, temperature, wine

Abstract.

Bottles of wine are seldomly stoppered with cork closures. This work aims at contributing to the understanding of the impact of bottleneck shape and storage temperature on the stoppers performance parameters. It was observed that natural and microagglomerated corks show different time and temperature dependence on the elastic memory, the wine absorption and the extraction forces. It was also determined that the extraction force of the microagglomerated corks is significantly affected by the bottleneck shape, with up to 15 daN differences. The on-going research intends to address the importance of the bottleneck shape on the performance metrics of the two cork types, natural and micro agglimerated.

INTRODUCTION

Cork stoppers are closure options for glass bottles promoting seal pressure from the inside of the bottleneck (figure 1). Cork stoppers can be made by cutting and processing the natural cork, or by manufacturing as micro agglomerated cork stoppers obtained by agglutinating cork André R. H. Pereira, Sofia A. Matos, José P. S. Aniceto, Ana C. Lopes Cardoso granules within a range of sizes from 0.25 mm to 8 mm, by an extrusion or molding process using binding substances and production aids [1].

Diversely combined factors are involved in the closure insertion into the bottleneck and its further sealing capacity. Bottlenecks are characterized by their manufactured dimensional tolerances. The dimensional relation of the internal bottleneck shape to the cork determines the sealing ability with the interfacial path being fixed by the length of the closure.

Cork shows viscoelastic properties [2], [3] under the deformation (strain) promoted inside a bottleneck. The elastic memory is also affected by the confinement time into a certain volume. Moreover, the mechanical behaviour is dependent of the water content and of the temperature [4], [5]. The advancement of liquid through cork in a bottle of wine has been described as a process consisting of three stages [8].

The use conditions can then impact the performance. The performance of corks can be assessed by the rebound recovery rate [6], compression and relaxation force [7], [8], extraction force [8], wine absorption and progression [9] and oxygen transfer [10], [11].

In the current work the goal is to bring insight into the impact of temperature and bottleneck profile on the corks performance in bottles stored for over one year.

METHODOLOGIES AND RESULTS

Two bottleneck profile typologies, three temperatures (room temperature for shelf storage simulation, 40°C to account for the travel of wine bottles in long distance hauls, and 8°C for fridge storage simulation) and two types of cork stopper (natural and micro agglomerated) were considered for the experimental design. The output variables aiming at measuring the performance of the cork closures were wine absorption, wine travel and rebound recovery rate.

A novel methodology adopting computer vision (Figure 2) and thermal images methods was used for evaluating performance, specifically for the wine absorption pattern and the diameter elastic memory after cork extraction.

In previous research it was highlighted that the time and temperature storage affect the cork elastic properties (Figure 3). Therefore, it is possible to postulate that the properties of the corks are determined by time and the temperature the stopper is subjected to in a certain volume. In a parallel experiment, it was confirmed that the extraction force is affected by the bottleneck shape by almost 15 daN when the opening of the bottle differs by less than 1.2 mm (Figure 4).

The ongoing research is designed to confirm the relevance of the bottleneck shape in the cork stoppers performance parameters.

FIGURES



Figure 1: representation of the seal pressure inside the bottleneck

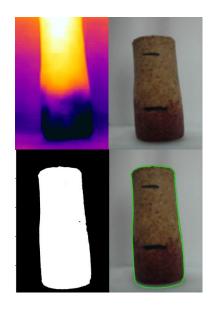
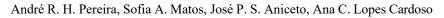


Figure 2: A) Thermal image captured with FLIR ONE PRO for wine absorption analysis, B) optical image, C) black and white image for computer vision process, D) final contour of the cork stopper for rebound recovery

rate



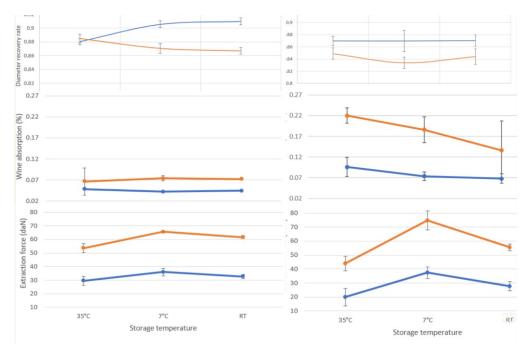
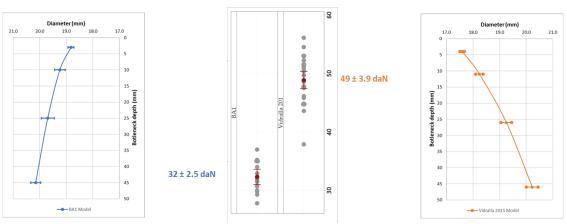


Figure 3: Preliminary results on the effect of temperature on microagglomerated (left) and natural (right) cork stoppers at 10-day and 180-day storage (The dots are the means and the vertical bars are standard deviations) after 10 days and 180 days of storage.



Individual Extraction Forces plot. At 95% Confidence level there is a difference of 16 daN.

Figure 4: The impact of bottleneck profile on the extraction force of a micro agglomerate cork stopper

REFERENCES

- [1] C. Liége, 'Código Internacional das Práticas Rolheiras'. Jun. 12, 2014. Accessed: Feb. 27, 2023.
 [Online]. Available: https://www.apcor.pt/wp-content/uploads/2016/05/CIPR PT 2016.pdf
- [2] L. J. Gibson, K. E. Easterling, and M. F. Ashby, 'The structure and mechanics of cork', *Proc. R. Soc. Lond. Math. Phys. Sci.*, vol. 377, no. 1769, pp. 99–117, Jun. 1981, doi: 10.1098/rspa.1981.0117.
- [3] H. Pereira, 'The Rationale behind Cork Properties: A Review of Structure and Chemistry', *BioResources*, vol. 10, no. 3, pp. 6207–6229, Jul. 2015, doi: 10.15376/biores.10.3.Pereira.
- [4] M. A. Fortes, M. E. Rosa, and H. Pereira, A cortiça. Lisboa: IST Press, 2004.
- [5] A. Lagorce-Tachon, T. Karbowiak, C. Paulin, J.-M. Simon, R. D. Gougeon, and J.-P. Bellat, 'About the Role of the Bottleneck/Cork Interface on Oxygen Transfer', *J. Agric. Food Chem.*, vol. 64, no. 35, pp. 6672–6675, Sep. 2016, doi: 10.1021/acs.jafc.6b02465.
- [6] M. E. Rosa and M. A. Fortes, 'Rate effects on the compression and recovery of dimensions of cork', *J. Mater. Sci.*, vol. 23, no. 3, pp. 879–885, Mar. 1988, doi: 10.1007/BF01153983.
- [7] M. Sánchez-González and D. Pérez-Terrazas, 'Dataset of mechanical properties from different types of wine stopper: Micro-agglomerated, natural cork and synthetic', *Data Brief*, vol. 21, pp. 2103–2109, Dec. 2018, doi: 10.1016/j.dib.2018.11.051.
- [8] A. Giunchi, A. Versari, G. P. Parpinello, and S. Galassi, 'Analysis of mechanical properties of cork stoppers and synthetic closures used for wine bottling', *J. Food Eng.*, vol. 88, no. 4, pp. 576–580, Oct. 2008, doi: 10.1016/j.jfoodeng.2008.03.004.
- [9] J. R. González-Adrados, F. González-Hernández, J. L. García de Ceca, M. J. Cáceres-Esteban, and M. C. García-Vallejo, 'Wine absorption by cork stoppers', *Span. J. Agric. Res.*, vol. 6, no. 4, p. 645, Dec. 2008, doi: 10.5424/sjar/2008064-356.
- [10] A. C. Lopes Cardoso, C. Rajbux, C. L. M. Silva, and F. Poças, 'Modelling oxygen ingress through cork closures. Impact of test conditions', *J. Food Eng.*, vol. 331, p. 111105, Oct. 2022, doi: 10.1016/j.jfoodeng.2022.111105.
- [11] P. Lopes, C. Saucier, P.-L. Teissedre, and Y. Glories, 'Main Routes of Oxygen Ingress through Different Closures into Wine Bottles', J. Agric. Food Chem., vol. 55, no. 13, pp. 5167–5170, Jun. 2007, doi: 10.1021/jf0706023.



7-8 September 2023, Espinho, Portugal

INVESTIGATION OF DISCOLORATION FACTORS BY SELECTIVE EXTRACTION OF CORK COMPONENTS OF QUERCUS VARIABILIS AND QUERCUS SUBER

Byeongho Kim1*, Hanna Park1, Yesun Kim1, Jae-Hyuk Jang2, Nam-Him Kim1 and Se-Yeong Park1,†

 ^{1*} Department of Forest Biomaterials Engineering, Kangwon National University, Chuncheon 24341, South Korea e-mail: skybeungho@kangwon.ac.kr
 ² FC KOREA LAND Co.,Ltd, R&D Center, Seoul 07271, South Korea e-mail: fc4u@daum.net
 [†]Department of Forest Biomaterials Engineering, Kangwon National University, Chuncheon 24341, South Korea e-mail: parksy319@kangwon.ac.kr

Abstract:

Cork is a biodegradable material that made of organic matters, so they can be damaged by environmental factors. When exposed to the external environment, wood or cork components are easily oxidized and decomposed by ultraviolet rays, and discoloration of the surface may occur. Therefore, this study conducted to observe the discoloration of the cork and find ways to protect it. Two kinds of *Quercus* species (*Quercus variabilis* and *Quercus suber*) with cork layers were used for UV exposure test. And, successive extraction of extracts, and suberin was performed to find the main factors related to discoloration. After UV test, the surfac colours of the extract-free and suberin-free corks turned gray unlike woods turned to yellowish or reddish. It was also observed that the discoloration proceeded quite rapidly. This was judged to be due to the characteristics of cork with different types and ratios of components (suberin) in wood.

Keywords: Cork discoloration, UV exposure test, Suberin, Extractives

INTRODUCTION

Cork is a bark tissue that exists in some tree species, and has recently been used as a road paving material, cork foam, and cork board. However, such products are biodegradable materials that made of organic matters, so they can be damaged by environmental factors. This phenomenon is known as wood deterioration. Among various factors related to wood deterioration, non-biological factors include temperature, humidity, and ultraviolet (UV) rays. When exposed to the external environment, wood components are easily oxidized and decomposed by ultraviolet rays, and discoloration of the wood surface (yellowing or graying) may occur [1][2][3]. Likewise, cork is a kind of wood-based materials, so protection of the surfaces is important for use.

Lignin, which is a component of wood, is known as a main factor of oxidation and is closely related to discoloration. UV forms a free radical in lignin structures and the free radicals react with oxygen to produce chromophores such as carbonyl and carboxyl groups [4][5]. However, unlike common woods, cork is mainly composed of suberin. Suberin has a structure in which fatty acids and lignin monomer structures are combined. Therefore, it was determined that it is necessary to observe the discoloration of the cork and find ways to protect it. For the research, artificial UV test was conducted using two *Quercus* spec ies with cork layers. And, we want to find the main factors related to the discoloration incork, so, successive extraction of extracts, and suberin was performed.

GENERALITIES

Quercus variabilis and *Quercus suber* were used as test samples. The specimens size was 25 mm \times 25 mm \times 5 mm.

For removing extracts in cork, solvent extraction was conducted following by dichloromethane, ethanol, and water for each 8 hours. And then, suberin was extracted using a 3% NaOCH3 solvent (Fig. 1). Samples at each stage were dried at room temperature and stored for UV test.

Accelerated weathering test was performed according to the ASTM G154 standard of nonmetallic materials. UV irradiation times was set to 8, 16, 24, 48, and 72 hours.

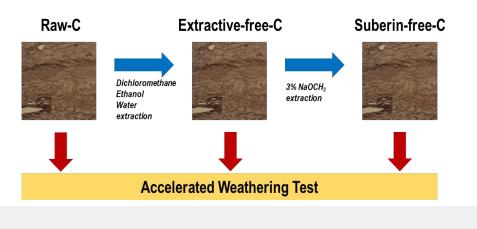
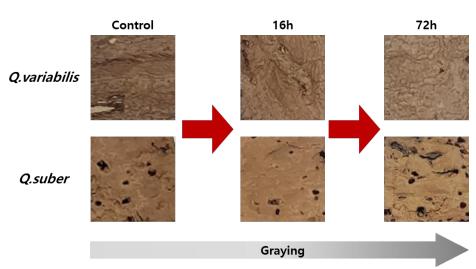


Fig. 1. Sample preparation for accelerated weathering test.

After UV test, it was observed that the surfac colours of the extract-free corks of *Q.variaibilis* and *Q.suber* turned slightly gray as shown in Fig. 2. A similar trend was also observed in suberin-free cork specimens (Fig. 3).

In case of common woods, colour changes to yellowing and reddening occurred mainly. But in cork, graying was clearly observed after the UV test. This was judged to be due to the characteristics of cork with different types and ratios of components in wood. A detailed analysis (FT-IR, colorimetric) is currently in progress.



Extract-Free-C

Fig. 2. Photographs of extract-free *Q.variabilis* and *Q.suber* corks after UV exposure test.

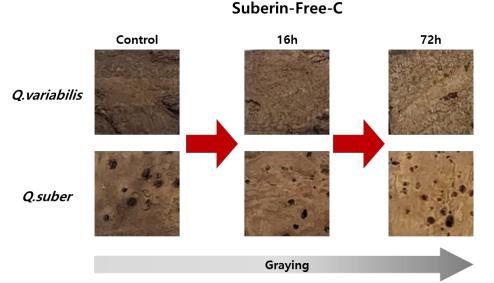


Fig. 3. Photographs of suberin-free Q.variabilis and Q.suber corks after UV exposure test.

REFERENCES

- [1] Cogulet, A., Blanchet, P., & Landry, V. (2016). Wood degradation under UV irradiation: A lignin characterization. Journal of Photochemistry and Photobiology B: Biology, 158, 184-191.
- [2] Van Nguyen, T. H., Nguyen, T. T., Ji, X., & Guo, M. (2018). Predicting color change in wood during heat treatment using an artificial neural network model. BioResources, 13(3), 6250-6264.
- [3] Hon, D. N. S., & Chang, S. T. (1984). Surface degradation of wood by ultraviolet light. Journal of Polymer Science: Polymer Chemistry Edition, 22(9), 2227-2241.
- [4] Derbyshire, H., & Miller, E. R. (1981). The photodegradation of wood during solar irradiation. Holz als Roh-und Werkstoff, 39(8), 341-350.
- [5] Wachter, I., Štefko, T., Rantuch, P., Martinka, J., & Pastierová, A. (2021). Effect of UV Radiation on Optical Properties and Hardness of Transparent Wood. Polymers, 13.



THERMOFORMING OF POLYLACTIC ACID AND CORK BIOCOMPOSITE SHEETS

Lisete Garrido Moutinho*, †, y, Eduardo Soares†, Martinho Oliveira*

*School of Design, Management and Production Technologies, University of Aveiro, Estrada do Cercal, nº449, 3720-509 Santiago de Riba-Ul, Oliveira de Azeméis, Portugal

[†]Amorim Cork Composites, Rua Comendador Américo Ferreira Amorim 260, 4535-186 Mozelos,

Portugal

^vCorresponding author; e-mail: l.moutinho@ua.pt

Keywords: Composite materials; Cork; Polylactic acid (PLA); Thermoforming

Abstract

Packaging is biggest application for plastics worldwide representing more than 40% of packaging market in 2022 [1]. For a period of time since the early stages of its development, PLA applications were limited to few specific applications like medical devices, due to its high cost. More recently, the introduction of new technologies and scale production have allowed to extend PLA application to more commodity areas like packaging. Thermoforming is a technology widely used by packaging industries to produce plastic based rigid packaging products from extruded sheets.

Cork polymer composites (CPC) are usually prepared through melt based technologies and currently they are one of the most propitious applications of cork to produce innovative products. Additionally, the production of CPC with bio-based thermoplastic polymers, such as polylactic acid (PLA) and poly(caprolactone) (PCL), has been studied as a potential solution towards sustainable composites development [2-5].

In this work, CPC with PLA as a thermoplastic matrix and 5% cork granules (w/w) were prepared by twin screw extrusion. After a drying step, these biobased CPC pellets were used to produce sheets by compression moulding with 1 mm thickness. The sheets were thermoformed in a vacuum thermoforming machine and the process parameters for this

process were optimized to achieve the best match of the sample with the mould used as represented in Figure 1. PLA sheets were also subjected to the same thermoforming process for comparison. The strain of the thermoformed sheets was analyzed by the deformation of the printed grids on the surface of each sheet before thermoforming (grids with 1x1 cm²). The thermoformed pieces were scanned by a 3D scanner (Artec model) and the distance between the grids were measured. The thickness was measured with a digital micrometer (Mitutoyo) on 40 points throughout the piece after thermoforming. A consistent relationship between thickness and strain was found. A thermal and morphological characterization was performed in all samples by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). With this work, the use of CPC sheets with PLA allowed to produce reliable thermoformed shapes which reinforces the possibility of enlarge CPC applications for thermoformed packaging solutions with PLA thermoplastic matrices.

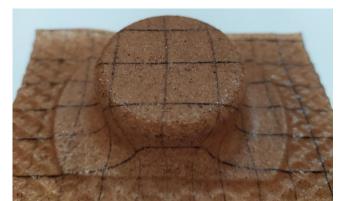


FIGURE 1 – Thermoformed sample from CPC sheet with PLA and 5% cork granules. The 1x1 cm2 grids used to measure the deformation are visible on the surface of the sample.

References

[1] Plastics Europe, The facts-2022. October 2022. <u>https://plasticseurope.org/wp-</u> <u>content/uploads/2022/12/PE-PLASTICS-THE-FACTS_FINAL_DIGITAL.pdf</u>(accessed February 2023)

- [2] Vilela C, Sousa AF, Freire CSR, Silvestre AJD, Pascoal Neto C. Novel sustainable composites prepared from cork residues and biopolymers. Biomass Bioenergy 2013;55:148–55.
- [3] Daver F, Lee KPM, Brandt M, Shanks R. Cork–PLA composite filaments for fused deposition modelling. Compos Sci Technol 2018;168:230–7.
- [4] Magalhães da Silva SP, Antunes T, Costa MEV, Oliveira JM. Cork-like filaments for

Additive Manufacturing. Addit Manuf 2020;34:101229.

[5] Ihamouchen C, Djidjelli H, Boukerrou A. Development and characterization of a new corkbased material. Mater Today Proc 2020;36:34–40.

INTER-TREE COMPETITION ANALYSIS IN SPANISH YOUNG CORK OAK PLANTATIONS

Mariola Sánchez-González*, María del Cuvillo García, Jose Ramón González-Adrados†

* Institute of Forest Science (ICIFOR-INIA, CSIC) Ctra. De La Coruña km 7,5 28040, Madrid, Spain e-mail: <u>msanchez@inia.csic.es</u>

[†] Universidad Politécnica de Madrid MONTES (School of Forest Engineering and Natural Resources) C/ José Antonio Novais, 10, 28040, Madrid, Spain e-mail: joseramon.gonzalez.adrados@upm.es

Keywords : diameter growth, growing space, competitors identification

Abstract

The objective of this study was to select and discuss indices to explain competition among cork oaks in unmanaged juvenile cork oak stands. This work was carried out in a plantation of *Quercus suber* L. located in the province of Toledo (Spain). The plantation was established in 1983 in 2×5 m spacing. In 2020, two plots of 0.6ha were installed and 406 trees were mapped and diameters at breast height, tree height, crown height and crown diameter were measured. A subsample of 45 trees were felled and ring width for each breast height section was measured. We tested widely used distance-independent and distance-dependent competition indices. These indices have been combined with different competitor selection methods. Pearson's correlation coefficient between the competition indices and diameter at breast height of the target tree and significance of correlations with the t test (p < 0.05) were used to evaluate the competition indices and the competitor selection methods. The relationship between competition indices and diameter at breast height of the torpetition indices and diameter at breast height was adjusted by regression analysis. Results provide insights into inter-tree competition and its role on diametric growth in juvenile cork oak forests.



DETERMINATION OF MOISTURE CONTENT IN LOOSE CORK GRANULATE USING NEAR INFRARED SPECTROSCOPY (NIRS)

Mariola Sánchez-González*, David Perez-Terrazas, Jose Ramón González-Adrados†

* Institute of Forest Science (ICIFOR-INIA, CSIC) Ctra. De La Coruña km 7,5 28040, Madrid, Spain e-mail: <u>msanchez@inia.csic.es</u>

[†] Universidad Politécnica de Madrid MONTES (School of Forest Engineering and Natural Resources) C/ José Antonio Novais, 10, 28040, Madrid, Spain e-mail: joseramon.gonzalez.adrados@upm.es

Abstract

The aim of this work was to develop models for the prediction of the moisture content of loose cork granulates using near-infrared spectroscopy. For this, 120 samples of 2.5 g of loose cork granulates free of anomalies were prepared, with a particle size between 0.5 - 1 mm. Batches of 40 samples were conditioned in a climatic chamber at 20°C and different relative humidity conditions (30%, 65% and 90%). Once stabilized, the NIRS spectra were obtained and the dry weight in the oven was determined, obtaining the moisture content of each sample. The results obtained (RMSECV= 0.30%, R2 =97.54 and RPD = 6.38) allow classifying the calibration equation as "good or very good". The results obtained demonstrate the viability of the NIRS technology for the determination of the moisture content of cork granulates quickly and accurately. To complete the model it would be necessary to develop calibration equations at different temperatures. The results obtained complete previous works on the characterization of cork granulates, and open up the possibility of obtaining important improvements in the quality control of this raw material.

PRODUCTION OF OXIDE FILMS WITH UV-FILTERING PROPERTIES ON CORK AND RUBBER - SAFEGUARDING FROM UV RADIATION AND MECHANICAL WEAR

B.Tiss^{*}, C. Mansilla[†], D. Martínez^{*,‡}, L. Cunha^{*}

* Physics Center of Minho and Porto Universities -CF-UM-UP, Campus de Gualtar, 4710-057 Braga, Portugal e-mail: <u>btiss@fisica.uminho.pt, dmartinez@fisica.uminho.pt, lcunha@fisica.uminho.pt</u>

[†] CTECHnano Coatings Technologies S.L., Tolosa Hiribidea 76, 20018, San Sebastián, Spain e-mail: <u>c.mansilla@ctechnano.com</u>

[‡] <u>Department of Materials Research and Technology, Luxembourg Institute of Science and Technology (LIST),</u> <u>28 avenue des Hauts-Fourneaux, Esch-sur-Alzette L-4362, Luxembourg</u>

Keywords: Composite materials, cork, rubber, MS and ALD techniques; TiO₂ and ZnO thin films; Sun test; Mechanical wear analysis

Abstract. Cork and rubber are natural materials that have been utilized in a wide range of applications for numerous years, including wine stoppers, flooring, footwear, and sports equipment. Both materials possess a polymeric organic nature that provides them with unique properties, which are highly valued by both industry and consumers. It is interesting to note that cork and rubber can also be combined as hybrid materials by creating cork particle compounds within vulcanized rubber, which can be utilized in the manufacturing of shoe soles and gaskets. This combination of materials can enhance their properties further, making them even more valuable in various industries. When exposed to sunlight or subjected to friction and/or mechanical wear, cork and rubber can exhibit signs of aging such as discoloration, scratches, and even craters. Maintaining the useful bulk characteristics of a material while enhancing its performance can be challenging when dealing with a sensitive or complex substrate, such as cork and rubber. However, depositing metallic oxide thin films (e.g. TiO2 and/or ZnO) that have high transmission in the visible region, high absorption in the UV range, and resistance to mechanical wear, may provide a suitable solution for addressing the aforementioned problems. Despite the challenges posed by the sensitive and complex substrate of cork and rubber, we were able to successfully deposit TiO2 [1], ZnO, and TiO2/ZnO thin films using two different deposition techniques: magnetron sputtering (MS) and atomic layer deposition (ALD). The B. Tiss, C. Mansilla, D. Martínez, L. Cunha

deposited TiO2 thin films exhibit high transmission in the visible range and block radiation with $\lambda < 320$ nm, although the ZnO thin films demonstrate superior behavior as they are capable of blocking radiation with $\lambda < 380$ nm. Sun exposure tests conducted on all of the deposited films revealed that the ZnO or TiO2/ZnO films provided the best protection. Furthermore, mechanical properties such as tensile strength, scratch resistance, and hardness were evaluated for both coated and uncoated materials.

REFERENCES

 D. Martínez-Martínez, B. Tiss, L.N. Glanzmann, D.J. Wolthuizen, L. Cunha, C. Mansilla, J.Th.M. De Hosson, "Protective films on complex substrates of thermoplastic and cellular elastomers: Prospective applications to rubber, nylon and cork," Surface and Coatings Technology, 442 (2022) 128405.



REPLACING POLYURETHANE IN AGGLOMERATED CORK USING A BIOBASED BINDER.

Lucie Quinquet*, Nathanaël Guigo, Luc Vincent, Nicolas Sbirrazzuoli†

* Université Côte d'azur Institut de chimie de Nice CNRS UMR 7272, Parc Valrose 06108 Nice CEDEX 2, France e-mail: <u>lucie.quinquet@univ-cotedazur.fr</u>

[†] e-mail: <u>nicolas.sbirrazzuoli@univ-cotedazur.fr</u>

Keywords: Composite materials, cork, biobased binder

Abstract.

Cork, with its versatile and intriguing qualities, is one of the most adaptable natural resources available to humankind. ^{1,2,3} Traditionally, its primary usage has been for natural cork stopper production, which, unfortunately, results in significant waste. ^{4,5} However, this waste can be repurposed into agglomerates that serve as both thermal and acoustic insulation, as well as cork stoppers and many other applications. ^{2,3} The primary concern regarding agglomeration is the use of polyurethane (PU) as a binder ^{2,6}, which contains isocyanates classified as carcinogenic, mutagenic, or toxic to reproduction. Furthermore, environmental regulations are on their way to constrain the use of some isocyanates. ⁷ As a result, this study is focused on replacing hazardous petrochemical binders with biobased and safer materials during the cork agglomeration process. To achieve the desired agglomeration of cork stoppers, a biobased diacid, sourced from fruits, was used to crosslink epoxidized linseed oil. In order to comply with industrial standards, it was important that the mixture cured at a maximum temperature of 150°C within 40 minutes. Additionally, the glue content needed to be less than 30w% of the sample, while maintaining or improving the properties of the final product. Solvent absorption tests, dynamic mechanical analysis, thermogravimetric analysis, tensile tests, and FT-IR were conducted on several samples, showing promising results.

Lucie Quinquet, Nathanaël Guigo, Luc Vincent and Nicolas Sbirrazzuoli.

REFERENCES

[1] H. Pereira, "Cork: biology, production and uses," 1st ed, Elsevier, 2007.

[2] L. Gil, "Cork Composites: A Review," *Materials*, vol. 2, no. 3, pp. 776–789, 2009.

[3] L. Gil., and C. Moiteiro, "Cork.", Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., 2003.

[4] N. Cordeiro, N. M. Belgacem, A. Gandini and C. P. Neto, "Cork suberin as a new source of chemicals: 2. Crystallinity, thermal and rheological properties," *Bioresource Technology*, vol. 63, no. 2, pp. 153–158, 1998.

 [5] I. M. Aroso, A. R. Araújo, R. A. Pires, R. L. Reis, "Cork: Current Technological Developments and Future Perspectives for this Natural, Renewable, and Sustainable Material," *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 12, pp. 11130–11146, 2017.

[6] K. Crouvisier-Urion, J. P. Bellat, R. D. Gougeon, T. Karbowiak, "Mechanical properties of agglomerated cork stoppers for sparkling wines: Influence of adhesive and cork particle size," *Composite Structures*, vol. 203, pp. 789–796, 2018.

[7] A. Cornille, R. Auvergne, O. Figovsky, B. Boutevin, S. Caillol, "A perspective approach to sustainable routes for non-isocyanate polyurethanes," *European Polymer Journal*, vol. 87, pp. 535–552, 2017.



PREDICTION OF SECONDARY CORK INDUSTRIAL QUALITY AND POROSITY BASED ON VIRGIN CORK CHARACTERISTICS

Diana I. Santos*and Joana A. Paulo*

 * University of Lisbon, School of Agriculture Forest Research Centre Tapada da Ajuda, 1349-017 Lisboa, Portugal
 e-mail: dianaisasantos@isa.ulisboa.pt; joanaap@isa.ulisboa.pt

Keywords: cork oak; *Quercus suber* L., CIELAB colour space, image analysis, cork defects, non-wood forest products, cork oak forest management, forest thinning.

Abstract.

The Portuguese official statistics from the National Forest Inventory demonstrate an increase of cork oak plantation area during the last 30 years. These young cork oak plantations may have initial stand densities higher than 800 trees ha⁻¹, values that are significantly high when compared with the mature stands [1]. The impact of planting such a higher number of trees per hectare has raised several questions by researchers and forest managers, namely regarding the intra specific competition. Currently, forest management plans defined for these plantations suggest that the first thinning should be performed a few years before the first cork extraction [2,3] in order to reduce the number of trees and as a result the tree competition. The trees to be removed are selected by visual observation (poor stem forms or signs of weakness) and/or, particularly in plantations, in a systematic way in order to achieve the required number of trees per hectare. Since no information regarding their potential as future cork producers is available, this operation may result in the removal of trees that would be good cork quality producers. The primary aim of this work is to research the possibility of using physical characteristics accessed in virgin cork sample, as predictors of secondary cork industrial quality and porosity.

Virgin cork samples were obtained from 3 different stands: A (n = 33), B (n = 18) and C (n = 15). Nine years after the first debarking, the same trees were resampled for secondary cork. Stand A is located in the Barrancos municipality, while stands B and C are located at Coruche municipality. Secondary cork samples were cooked at 100 °C for 1 h, then dried at room temperature in a well-ventilated place, following the industrial process carried out by the cork industry. Secondary cork samples were then visually classified regarding industrial cork quality

Diana I. Santos and Joana A. Paulo

classes by an experienced operator. Cork samples were therefore classified from 1st quality, the better cork, to 7th ('refugo' in Portuguese), the cork with lowest quality. Cork colour was determined in virgin and secondary cork samples, based on CieLab colour space with a Konica Minolta colorimeter. This variable was accessed in the radial and transversal directions of the cork samples, and also in the cork sample back ('costa' in Portuguese) and belly ('barriga' in Portuguese). Virgin and secondary samples were then polished on a sander with P100 sandpaper. This procedure is crucial to allow cork porosity determination, that was done using the analySIS software for each cork sample (virgin and secondary cork samples). The data analysis was carried out in order to consider two different aspects of the data set. The Pearson correlation coefficient (r) was determined to access the correlation of cork colour and porosity values, obtained in virgin and secondary cork samples. A t-test comparison was carried out to the average values of colour and porosity from the virgin cork samples, when the data set was grouped by industrial cork quality classes determined in secondary cork samples. The t-tests were also carried out when the data set was grouped considering only three cork quality classes: Good cork (1st, 2nd and 3rd cork quality classes), average cork (4th and 5th cork quality classes) and poor cork (6th and 7th cork quality classes).

Results showed that colour parameters, in particular L^* , measured in virgin cork distinguish the best quality cork in all sample directions when considering grouped 1st, 2nd and 3rd cork quality classes from the remaining cork classes. The colour parameter a^* measured in virgin cork differentiates good cork quality from average cork and poor cork in the radial and transversal directions, while parameter b^* distinguishes good cork quality from poor cork quality. The correlation analysis between the porosity values obtained for virgin cork and secondary cork presented a R²=0.19, which indicates a low but statistically significant correlation between the two variables.

REFERENCES

- [1] ICNF, IFN6 "Áreas dos usos do solo e das espécies florestais de Portugal continental. Resultados preliminares", Instituto da Conservação da Natureza e das Florestas, pp. 33, Lisboa, 2013 (available only in Portuguese).
- [2] G. Montero and I. Cañellas, "Manual de reforestación y cultivo de alcornoque (*Quercus suber* L.)", Ministerio de Agricultura, Pesca y Alimentación, Instituto Nacional de Investigación y Tecnología Agrária y Alimentaria, Madrid, 1999.
- [3] F. Pulido, P. Campos, G. Montero, "La gestión forestal de las dehesas", Instituto del corcho, la madera y del carbón, Junta de Extremadura, Mérida, 2003.



STUDY OF THE AROMATIC PROFILE OF QUERCUS SUBER L. Jové, P^{1*}, De Nadal, R² and Verdum Virgos, M³.

 ^{*}¹Fundació Institut Català del Suro Catalan Cork Institute Foundation
 Miquel Vincke i Meyer, 13, 17200 Palafrugell, Spain e-mail: <u>mverdum@icsuro.com</u> ²J.VIGAS R&D Department
 Josep Anselm Clavé, 49, 17200 Palafrugell e-mail: <u>raquel@jvigas.com</u>

Keywords: Quercus suber L, cork, aroma, volatile compounds

Abstract. Cork a natural material that is associated with sustainability due to its way of extraction it does not damage the tree. This material has other beneficial properties such as capacity to prevent soil desertification or protect the biodiversity around it. Also, cork contains aromatic compounds with beneficial properties that can be used to benefit other sectors such as food, pharmaceutical or cosmetic. An innovative and

solvent free methodology was developed to study the aromatic profile of Quercus suber L. The volatile compounds from cork were extracted, preconcentrated and detected by thermal desorption coupled to gas chromatography (TD-GCMSMS). The optimal conditions were achieved when cork was brought to 220°C during 10 minutes. 68 different compounds were detected in samples from Catalonia (51), Sardinia (43) and Extremadura (37) and were grouped according to their chemical structures in 8 families of compounds. The application of a thermal treatment in Sardinia samples has increased the number and quantity of volatile compounds that have been extracted. All the samples showed: aromatic compounds (66.8%) and aliphatic alcohols (22.2%) were the most abundant families. Vanillin (39.3%), docosanol (16.9%) and coniferyl aldehyde (7.7%) were the most abundant compounds. In conclusion, the developed methodology allows the extraction of a wide range of

volatile compounds. Quercus suber L. contains valuable volatile compounds to be proposed as flavoring agents in other industries such as cosmetic or food.

INTRODUCTION

Quercus suber L. or cork oak has ecological and social value. Cork oak constitutes a unique ecosystem with an important biodiversity associated. Also, it is responsible for thousands of businesses since it is the source of the cork stopper sector. Due to its physical properties such as high flexibility, elasticity, compressibility or impermeability to liquid, cork stoppers are a perfect closure for sealing still and sparkling wines (1). This combination of cork properties depend on some factors such as its chemical composition or cellular structure (2).

Cork of *Quercus suber* L. is composed of suberin, lignin, polysaccharides, extractives and other minor components (2,3). Extractives comprise a heterogeneous group of molecules mainly aliphatic, triterpenic and phenolic compounds (4, 5) that can be extracted from cork stoppers by hydroalcoholic solution. Nowadays, there is evidence that some of these extractives or volatile organic compounds (VOCs) of cork can positively contribute to the aroma, color or astringency of wine (6-8). Also, some of them are associated with health benefits related to antioxidative activities (10-12) among others.

Aroma is one of the most important attributes in vegetal samples and a large number of VOCs have been reported in cork samples including alcohols, fatty acid ethyl esters, acetic acid esters, among others (9, 13-19). Some of them are associated with the presence of specific microflora on the tree and/or cork slabs (14, 20-21) and others are the result of reactions related to the reestructuracion of some macromolecular compounds such as lignin (5, 14, 22) and possibly also suberin (6, 17). It seems that volatile compounds are different according to the cork's origin for example in the case of cork bark compared to cork stoppers

(1). Likewise, the level of porosity in natural cork stoppers can be at influence (9). Cork granules also shower higher amounts of VOCs than cork stoppers (11). The determination of the type and amount of volatile compounds present in samples of cork from different geographical origin has not yet been studied.

A wide range of analytical methods have been developed for the determination of VOCs in vegetal samples and most of them employ the gas chromatography (GC) for separation of compounds and mass spectrometry (MS) for their detection. In addition, a previous stage of sample preparation that can include extraction and/or VOCs preconcentration process before chromatographic analysis is also necessary due to its low concentration in samples.

Sample preparation techniques are usually carried out using different solvents depending on

the chemical properties of selected compounds to facilitate their extraction from the solid matrix. Nowadays, techniques such as head space extraction coupled with solid phase micro extraction (HS-SPME) or direct sample introduction (DSI) are a sustainable alternative because they are a solvent free, rapid and simple analytical method that precludes sample preparation. Both methodologies have been widely used for screening and qualitative analysis of a wide range of VOCs extracted from liquid and solid samples.

HS-SPME methodology has already been used for the analysis of volatile compounds in cork material (6, 7, 9, 23). On the other hand, DSI is widely used in the extraction of pesticides (24-26), atmospheric aerosols (27), polycyclic aromatic hydrocarbons (28), organic chemicals in fish oils (29) and haloanisole compounds in cork stoppers (30). It is suitable for

complex matrices with a large number of volatile compounds because of its differences in polarity, volatility or molecular weight. Due to these characteristics, DSI is useful for VOCs only changing the extraction and desorption factors such as temperature, time or flow. The use of this methodology for VOCs extraction of cork samples has not yet been applied.

An innovative and solvent free methodology to study the VOCs from *Quercus suber* L. was developed. TD GCMS was used to extract and analyze VOCs in cork samples. Extraction (time and temperature) and preconcentration (trap settings) conditions were evaluated in order to extract the greatest number of volatile compounds with higher concentration. Cork from Extremadura, Cataluña and Sardinia were analyzed. Sardinia samples were submitted at a thermal treatment to check the effect of temperature in the type of extracted VOCs. This knowledge is useful for sectors such as food, cosmetic or pharmaceutical those are searching valuable compounds to improve their products.

REFERENCES

- [1] Maga, J. A. and Puech, J.L. (2005). Cork and alcoholic beverages. Food Reviews International, 21(1), 53–68.
- [2] Pereira, H. (1988). Chemical composition and variability of cork from *Quercus suber* L.
 Wood Science and Technology, 22(3), 211–218.
- [3] Pereira, H. (2007). The chemical composition of cork. In Cork (pp. 55–99). Elsevier.
- [4] Rocha, S., Coimbra, M., Delgadillo, I. (2004). Occurrence of furfuraldehydes during the processing of *Quercus suber* L. cork. Simultaneous determination of furfural, 5hydroxymethylfurfural and 5-methylfurfural and their relation with cork polysaccharides. Carbohydrate Polymers, 56(3), 287–293.

- [5] Rocha, S. M., Ganito, S., Barros, A., Carapuça, H. M., Delgadillo, I. (2005). Study of cork (from *Quercus suber* L.) wine model interactions based on voltammetric multivariate analysis. Analytica Chimica Acta, 528(2), 147–156.
- [6] Moreira, N., Lopes, P., Cabral, M., Guedes de Pinho, P. (2016). HS-SPME/GC-MS methodologies for the analysis of volatile compounds in cork material. European Food Research and Technology, 242(4), 457–466.
- [7] Pinto, J., Oliveira, A. S., Lopes, P., Roseira, I., Cabral, M., Bastos, M. de L., Guedes de Pinho, P. (2019). Characterization of chemical compounds susceptible to be extracted from cork by the wine using GC-MS and 1H NMR metabolomic approaches. Food Chemistry, 271, 639–649.
- [8] Oliveira, A. S., Furtado, I., Bastos, M. de L., Guedes de Pinho, P., Pinto, J. (2020). The influence of different closures on volatile composition of a white wine. Food Packaging and Shelf Life, 23.
- [9] Furtado, I., Oliveira, A. S., Amaro, F., Lopes, P., Cabral, M., de Lourdes Bastos, M., Pinto, J. (2021). Volatile profile of cork as a tool for classification of natural cork stoppers. Talanta, 223, 121698.
- [10] Fernandes, A., Fernandes, I., Cruz, L., Mateus, N., Cabral, M., de Freitas, V. (2009). Antioxidant and Biological Properties of Bioactive Phenolic Compounds fromQuercus suberL. Journal of Agricultural and Food Chemistry, 57(23), 11154–11160.
- [11] Mislata, A. M., Puxeu, M., & Ferrer-Gallego, R. (2020). Aromatic potential and bioactivity of cork stoppers and cork by-products. Foods, 9(2), 133.
- [12] Mota, S., Pinto, C., Cravo, S., Rocha e Silva, J., Afonso, C., Sousa Lobo, J. M., Tiritan, M. E., Cidade, H., & Almeida, I. F. (2022). *Quercus suber*: A Promising Sustainable Raw Material for Cosmetic Application. Applied Sciences, 12(9), 4604.
- [13] Mazzoleni V, Caldentey P, Careri M, Mangia A, Colagrande O. (1994). Volatile components of cork used for production of wine stoppers. Am J Enol Viticult, 45, 401– 406.
- [14] Rocha, S., Delgadillo, I., & Ferrer Correia, A. J. (1996). GC-MS Study of Volatiles of Normal and Microbiologically Attacked Cork from *Quercus suber* L. Journal of Agricultural and Food Chemistry, 44(3), 865–871.
- [15] Rocha, S., Delgadillo, I., Ferrer Correia, A. J., Barros, A., Wells, P. (1998). Application of an electronic aroma sensing system to cork stopper quality control. Journal of Agricultural and Food Chemistry, 46(1), 145–151.

- [16]Caldentey, P., Fumi, M. D., Mazzoleni, V., Careri, M. (1998). Volatile compounds produced by microorganisms isolated from cork. Flavour and Fragrance Journal, 13(3), 185–188.
- [17] Coquet, C., Ferré, E., Peyronel, D., Dal Farra, C., Farnet, A. M. (2008). Identification of new molecules extracted from *Quercus suber* L. cork. Comptes Rendus Biologies, 331(11), 853–858.
- [18] Azevedo, J., Fernandes, I., Lopes, P., Roseira, I., Cabral, M., Mateus, N., Freitas, V. (2014). Migration of phenolic compounds from different cork stoppers to wine model solutions: Antioxidant and biological relevance. European Food Research and Technology, 239(6), 951–960.
- [19] Amaro, F., Almeida, J., Oliveira, A. S., Furtado, I., Bastos, M. de L., Guedes de Pinho, P., Pinto, J. (2022). Impact of cork closures on the volatile profile of sparkling wines during bottle aging. Foods, 11(3), 293.
- [20] Alvarez-Rodríguez, M. L., López-Ocana, L., López-Coronado, J. M., Rodríguez, E., Martínez, M. J., Larriba, G., Coque, J. J. R. (2002). Cork taint of wines: role of the filamentous fungi isolated from cork in the formation of 2, 4, 6-trichloroanisole by O methylation of 2, 4, 6-trichlorophenol. Applied and environmental microbiology, 68(12), 5860-5869.
- [21]Barreto, M. C., Vilas Boas, L., Carneiro, L. C., San Romão, M. V. (2011). Volatile compounds in samples of cork and also produced by selected fungi. Journal of agricultural and food chemistry, 59(12), 6568-6574.
- [22] Rudnitskaya, A., Delgadillo, I., Rocha, S. M., Costa, A. M., Legin, A. (2006). Quality evaluation of cork from *Quercus suber* L. by the electronic tongue. Analytica chimica acta, 563(1-2), 315-318.
- [23] Neto, P. V., Rocha, S. M., Silvestre, A. J. (2007). Simultaneous headspace solid phase microextraction analysis of off-flavour compounds from *Quercus suber* L. cork. Journal of the Science of Food and Agriculture, 87(4), 632–640.
- [24] Lehotay, S. J. (2000a). Analysis of pesticide residues in mixed fruit and vegetable extracts by direct sample introduction/gas chromatography/tandem mass spectrometry. Journal of AOAC INTERNATIONAL, 83(3), 680–697.
- [25] Lehotay, S. J. (2000b). Analysis of pesticide residues in mixed fruit and vegetable extracts by direct sample introduction/gas chromatography/tandem mass spectrometry. Journal of AOAC INTERNATIONAL, 83(3), 680–697.

- [26] Čajka, T., Maštovská, K., Lehotay, S. J., Hajšlová, J. (2005). Use of automated direct sample introduction with analyte protectants in the GC–MS analysis of pesticide residues. Journal of Separation Science, 28(9–10), 1048–1060.
- [27] Falkovich, A. H., Rudich, Y. (2001). Analysis of semivolatile organic compounds in atmospheric aerosols by direct sample introduction thermal desorption GC/MS. Environmental Science & amp; Technology, 35(11), 2326–2333.
- [28] Bates, M., Bruno, P., Caputi, M., Caselli, M., de Gennaro, G., Tutino, M. (2008). Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS. Atmospheric Environment, 42(24), 6144–6151.
- [29] Hoh, E., Lehotay, S. J., Mastovska, K., Ngo, H. L., Vetter, W., Pangallo, K. C., Reddy, C. M. (2009). Capabilities of direct sample introduction-comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry to analyze organic chemicals of interest in fish oils. Environmental Science; Technology, 43(9), 3240–3247.
- [30] Cacho, J. I., Nicolás, J., Viñas, P., Campillo, N., & Hernández-Córdoba, M. (2016). Direct sample introduction-gas chromatography-mass spectrometry for the determination of haloanisole compounds in cork stoppers. Journal of Chromatography A, 1475, 74–79.



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

STUDY OF CORK FROM *QUERCUS SUBER* WITH AND WITHOUT YELLOW SPOT: AROMATIC FRACTION AND CELLULAR STRUCTURE

Jové, P1*, De Nadal, R², Verdum Virgos¹, M. and Fiol, N³

¹ Fundació Institut Català del Suro Catalan Cork Institute Foundation Miquel Vincke i Meyer, 13, 17200 Palafrugell, Spain e-mail: <u>pjove@icsuro.com</u> ² J.VIGAS

R&D Department

Josep Anselm Clavé, 49, 17200 Palafrugell

e-mail: raquel@jvigas.com

³Departament d Enginyeria Química, Agrària i Tecnologia Agroalimentària, Universitat de Girona, Avda Lluís Santaló, 17003 Girona, Spain e-mail: <u>nuria.fiol@udg.edu</u>

Keywords: Quercus suber L, cork, yellow spot, volatile compounds, cellular structure

Abstract. Cork is widely used for the production of cork stoppers especially for wines with a long-term storage. A considerable effort has been made to improve the quality control during the manufacture of cork stoppers. Visual checks on cork barks are done to remove cork with yellow spots because its presence is related to the appearance of off flavours and could affect its mechanical properties. Cork with yellow spot is not used for cork stoppers production. The effect of the presence of yellow spots in samples of cork from Quercus suber was studied in relation to volatile compounds and the influence on the cellular structure. The volatile compounds of cork were analyzed using thermal desorption combined with gas chromatography (TD-GCMSMS). This

methodology had identified 58 compounds in cork samples. All of the samples showed: aromatic compounds (43.1%) followed by carboxylic acids (10.3%), aliphatic alcohols (6.9%), alkanes (6.9%), ester (6.9%) and terpenoids (6.9%). Vanillin was the most abundant compound (62.8%) followed by isoeugenol (7.1%). Chlorated compounds such as 1,2,4,5-tetrachloro-3,6-dimethoxybenzene, 2,4,5-Trichloroanisole and 2,4,5trichlorophenol had been identified in cork with yellow spot. Cellular structure of cork seems to be influenced by the presence of yellow spots, it shows: decrease the corrugations in the cell wall and the overall cell organization seems to be disrupted. These results allows to understanding some changes produced in cork by the presence of yellow spot.

Introduction

The cork oak (*Quercus suber* L.) is the dominant species of some agroforestry systems in Iberian Peninsula (Portugal and Spain, mainly) and are economically sustained by the production of cork. Cork is mainly used to obtain cork stoppers or closures for still and sparkling wine due to its beneficial properties: compressibility, elasticity, impermeability to air and liquid and the capacity to adhere to a glass surface. Because of these set of properties, cork has become relevant in several industries. These properties are the result of the combination of its chemical composition and cellular structure (1,2).

Cork undergoes through different quality controls to ensure the smooth functioning of cork stoppers. After extracting the cork and before starting the phases of cork stoppers manufacturing, a visual check of cork slabs is done occasionally, cork may include features of biological or external origin that impact in the quality to a degree that depends on their type and extent (3). Fractures, inclusions or stains such as yellow spot (YS) or "Mancha Amarela" are some of them. In the industrial manufacturing only the best quality slabs of cork are used and every natural cork stopper produced is visually checked and graded into several visual classes. ISO 17727:2012 describes the quality control sampling plans for the receipt and shipping of ready-to-use cylindrical stoppers in semi-worked or finished cork used for still wines. All the cork materials that are not suitable for cork stoppers production (or raw cork material) are used to produce cork agglomerates as boards or sheets for the production of flooring or rubber composites (3).

Jové, P, De Nadal, R, Verdum Virgos, M. and Fiol, N.

The presence of yellow spot (YS) is a defect caused by the presence of *Armillaria mellea* or a basidiomycete that grows in ligninolytic materials (3-5). In cork, this fungal attack causes the presence of regions that acquires a white-yellowish discoloration with a characteristic odour. Also, chemical and physical changes in cork with yellow spots are also reported (6,7). These changes could affect mechanical and structural properties of cork and, consequently, it may be closely related to the production of off flavours (4, 7-9). The effect of the presence of YS in chemical composition of cork is already described attributing lignin and polysaccharides content decreases (6). Also, corks with YS contain a smaller amount of lignin and pectic polysaccharides that is responsible for changes in the cork cell wall (5). These changes in the chemical composition are responsible for the differences in cellular structure between cork with and without YS: the cellular structure of cork with YS is composed by deformed and wrinkly cells with cell wall separation due to the degradation of the middle lamella pectic polysaccharides (5). This fact contributes to the availability of a nutrient source in the attacked cork that can be used by other microorganisms (5).

The study of the volatile compounds present in attacked cork allows researchers to further the identification of chemical modifications that occurs in cork polymers. The degradation of lignin seems to be related to the presence of a largest concentration of phenols, vanillin, benzaldehide, benzyl alcohol and chlorinated compounds (4). Also, cork with YS contains other volatile components resulting from microbial metabolism with possible consequences in the cork aroma composition (10).

Several compounds have been reported in cork samples such as alcohols, aldehydes, aliphatic hydrocarbons, ketones, esters, ethers, furans, among others (11-15). Some of them are associated with the presence of specific microflora on the tree and/or cork slabs (4, 16-18) and others are the result of reactions related to the reestructuracion of some macromolecular compounds such as lignin (4,7,8) and possibly also suberin (19, 20). It seems that the identified compounds are different according to the cork sources for example in the case of cork bark compared to cork stoppers (12). The study of the volatile compounds of cork with and without YS will bring other viewpoint to understand the changes brought about by the presence of this fungus in cork.

The slabs with YS are not used for cork stopper production due to the decrease of cork quality. Thus, the study of the changes associated with the presence of YS in cork is important for a better understanding of its features. The aim of this study is to obtain more information about the changes in structural and volatile compounds associated with the presence of YS onto

cork.

REFERENCES

[1] Pereira, H., Emília Rosa, M., Fortes, M. A. (1987). The cellular structure of cork from *Quercus suber* L. IAWA Journal, 8(3), 213–218.

[2] Pereira, H. (1988). Chemical composition and variability of cork from *Quercus suber* L. Wood Science and Technology, 22(3), 211–218.

[3] Pereira, H. (2011). Cork: Biology, production and uses. Elsevier.

[4] Rocha, S., Delgadillo, I., Ferrer Correia, A. J. (1996a). GC–MS Study of Volatiles of Normal and Microbiologically Attacked Cork from *Quercus suber* L. Journal of Agricultural and Food Chemistry, 44(3), 865–871.

[5] Rocha, S. M., Coimbra, M. A., Delgadillo, I. (2000). Demonstration of Pectic Polysaccharides in Cork Cell Wall from *Quercus suber* L. Journal of Agricultural and Food Chemistry, 48(6), 2003–2007.

[6] Carriço, S. M. da R. S. (1997, January 1). Estudo da composição química, da estrutura celular e dos componentes voláteis da cortiça de *Quercus suber* L.

[7] Rocha, S. M., Ganito, S., Barros, A., Carapuça, H. M., Delgadillo, I. (2005). Study of cork (from *Quercus suber* L.) wine model interactions based on voltammetric multivariate analysis. Analytica Chimica Acta, 528(2), 147–156.

[8] Rudnitskaya, A., Delgadillo, I., Rocha, S. M., Costa, A. M., Legin, A. (2006). Quality evaluation of cork from *Quercus suber* L. by the electronic tongue. Analytica Chimica Acta, 563(1–2), 315–318.

[9] Neto, P. V., Rocha, S. M., Silvestre, A. J. (2007). Simultaneous headspace solid phase microextraction analysis of off-flavour compounds from *Quercus suber* L. cork. Journal of the Science of Food and Agriculture, 87(4), 632–640.

[10] Caldentey, P., Fumi, M. D., Mazzoleni, V., Careri, M. (1998). Volatile compounds produced by microorganisms isolated from cork. Flavour and Fragrance Journal, 13(3), 185–188.

[11] Mazzoleni, V., Caldentey, P., Careri, M., Mangia, A., Colagrande, O. (1994). Volatile components of cork used for production of wine stoppers. American Journal of Enology and Viticulture, 45(4), 401–406.

[12] Maga, J. A., Puech, J.L. (2005). Cork and alcoholic beverages. Food Reviews International, 21(1), 53–68.

Jové, P, De Nadal, R, Verdum Virgos, M. and Fiol, N.

[13] Culleré, L., Cacho, J., Ferreira, V. (2009). Comparative study of the aromatic profile of different kinds of wine cork stoppers. Food Chemistry, 112(2), 381–387.

[14] Moreira, N., Lopes, P., Cabral, M., Guedes de Pinho, P. (2016). HS-SPME/GC-MS methodologies for the analysis of volatile compounds in cork material. European Food Research and Technology, 242(4), 457–466.

[15] Furtado, I., Oliveira, A. S., Amaro, F., Lopes, P., Cabral, M., Bastos, M. de L., Guedes de Pinho, P., Pinto, J. (2021). Volatile profile of cork as a tool for classification of natural cork stoppers. Talanta, 223, 121698.

[16] Pereira, C. S., Marques, J. J. F., San Romão, M. V. (2000). Cork taint in wine: Scientific knowledge and public perception — A critical review. Critical Reviews in Microbiology, 26(3), 147–162.

[17] Alvarez-Rodríguez, M. L., López-Ocaña, L., López-Coronado, J. M., Rodríguez, E., Martínez, M. J., Larriba, G., Coque, J.-J. R. (2002). Cork taint of wines: Role of the filamentous fungi isolated from cork in the formation of 2,4,6-trichloroanisole by O methylation of 2,4,6-trichlorophenol. Applied and Environmental Microbiology, 68(12), 5860–5869.

[18] Barreto, M. C., Vilas Boas, L., Carneiro, L. C., San Romão, M. V. (2011). Volatile compounds in samples of cork and also produced by selected fungi. Journal of agricultural and food chemistry, 59(12), 6568-6574.

[19] Coquet, C., Ferré, E., Peyronel, D., Dal Farra, C., Farnet, A. M. (2008). Identification of new molecules extracted from *Quercus suber* L. cork. Comptes Rendus Biologies, 331(11), 853–858.

[20] Moreira, N., Lopes, P., Cabral, M., Guedes de Pinho, P. (2016). HS-SPME/GC-MS methodologies for the analysis of volatile compounds in cork material. European Food Research and Technology, 242(4), 457–466.



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

THE INFLUENCE OF THE PRODUCTION PROCESS ON THE NATURAL CORK STOPPERS PERMEABILITY AND ITS IMPACT ON STILL WINE AGING

Verdum Virgos, M*. Jové Martín, P*

 * Fundació Institut Català del Suro Catalan Cork Institute Foundation
 Miquel Vincke i Meyer, 13, 17200 Palafrugell, Spain e-mail: <u>mverdum@icsuro.com</u>

Keywords: permeability, OTR, natural cork stopper, chemiluminescence,.

Abstract.

The importance of oxygen role during aging process of wine has been long known. Many articles evaluating oxygen inlet for different wine stoppers have been published. However, none of these have studied the impact of the natural cork stoppers production process impact over oxygen inlet. At the moment, a standardized methodology widely accepted for measuring the oxygen transfer rate (OTR) and/or oxygen permeability of the stopper does not exist.

Thus, this article aims to test how some production process of natural cork stoppers impact on the stoppers permeability using chemiluminescence methodology and how also this affects wine ageing.

In this study it has been seen that some of its processes such as the application of a surface treatment modify the permeability of the stopper. Surface plays an important role in the corks stoppers production and allows an easier insertion and extraction of the stopper into the bottle, avoiding leaks and homogenizing the stoppers.

It was shown that the cork stoppers sample with surface treatment B had three times higher oxygen transfer rate than the cork stoppers sample with surface treatment A after one year of evolution. The two groups of stoppers had the same in terms of dimensions, density, visual class, batch and manufacture, the only difference between them was the surface treatment used. A red wine was corked with these two types of cork stoppers and its evolution was monitored up to 30 months of ageing. Differences were observed in the evolution of the wines both in

certain oenological parameters such as the free SO_2 , the colour and the evolution of the polyphenols as well as at the sensory level. The wine corked with the stoppers of treatment B presented a faster evolution and a higher valuation in the sensory tastes of months 9th and 12th, while from the 18th month it presented an over evolution and the score was below that of the wine with the corks of treatment A.

The data collected in this study shows that the differences observed with the chemiluminescence methodology of cork permeability test at a laboratory level are transferred to wine at the cellar. Therefore, it paves the way to standardize chemiluminescence as a methodology for permeability testing of cork stoppers. This opens a new field for the regulation of the permeability of natural cork stoppers by type of surface treatment applied.



NOVEL SUSTAINABLE ALTERNATIVES FOR THE STUDY OF CHEMICAL COMPOSITION OF CORK

Verdum Virgos, M*. Jové Martín, P*

* Fundació Institut Català del Suro
 Catalan Cork Institute Foundation
 Miquel Vincke i Meyer, 13, 17200 Palafrugell, Spain
 e-mail: <u>mverdum@icsuro.com</u>

Keywords: Chemical composition, cork extractive, cork, soxhlet, ASE, MAE

Abstract. Cork is a natural and renewable material extracted from the cork oak, Quercus suber L. Its physical and mechanical properties are a result of the cellular structure and chemical composition of the plant wall. Chemically the composition of cork is principally dominated by the presence of suberin as the main structural cell wall component and by its close association with the other components. The usual chemical analysis of cork has been adapted from wood and other lignocellulosics analytical methods. This traditional method is based on a very long methodology that makes it difficult to implement it as a routine quality test in a cork manufacture. Microwave assisted extraction (MAE) and accelerated solvent

Verdum Virgos, M. Jové Martín, P

extraction (ASE) have been explored, such as alternatives system for the traditional method. The percentages of extractives obtained by MAE are lower than the percentages obtained by means of the classical composition. However, the percentages of suberin are very similar in both methods: 46.39% in the case of the classical composition and 45.11% in the case of microwave-assisted extraction. No significant differences have been found between the content of extractives in dichloromethane, ethanol and water obtained by ASE with the results obtained with the classical methodology. MAE and ASE are faster methods, use less solvent and provide more reproducible results than the classical chemical composition methodology. These data pave the way for novel sustainable alternatives for the studies of chemically the composition of cork.

INTRODUCTION

Cork comes from the outer bark of the cork oak, *Quercus suber* L. Cork is a natural and renewable material extracted mainly in the Western Mediterranean area [1]. The physical and mechanical properties of cork are a result of the cellular structure and chemical composition of the plant wall (suberin, lignin, and polysaccharides).

Chemically the composition of cork is dominated by the presence of suberin as the main structural cell wall component and by its close association with the other components. This results is a difficult methodological approach to comprehensively analyse of cork in terms of its chemical components. The composition of cork began to be studied by Brugnatelli in 1787

[2]. From then until today the composition of cork and its macromolar structure are still being studied and there are still no clear models. The methodology used in determining the chemical composition as well as other aspects such as the origin, the physiological state or the number of specimens can condition the results. The structural components of the cell wall by order of relative importance are: suberin (50% approx.), lignin (20-25%), and the polysaccharides (about 20%), cellulose, and hemicelluloses; the extractive (14-18%), which include lipid and phenolic substances and inorganic components (1-2%) [2; 3] (figure 1).

The usual chemical analysis of cork has been adapted from wood and other lignocellulosics analytical methods. The conventional approach to the chemical characterisation of cork is to report its summative chemical composition. The analysis of the chemical composition of traditional cork is based on a sequential determination [4] of the ash content (TAPPI 211), extractives (TAPPI 204/207/ [5]), suberin [6] Klason lignin and acid soluble lignin [7] and

Verdum Virgos, M. Jové Martín, P

holocellulose (TAPPI 222/250).

Thus, the traditional method is based on a three-step serial extraction using the soxhlet. It begins with a soxhlet with an organic solvent with apolar characteristics (dichloromethane) for the directed extraction of compounds of a ceroid nature for 6 hours. It follows with a second soxhlet extraction with alcohol that lasts 8 hours and, finally, a soxhlet extraction with water form 16 to 24 hours or, an extraction with a methanol and water solution can also be given. With these extractions, polyphenols are mostly extracted. With the sample free of extractives, the suberin content is determined, based on alkaline methanolysis (3 hours), followed by acidification and rotaevaporation (1 hour), resuspension with two solvents, and decantation to obtain suberin in the organic phase (1 hour). With the suberin-free fraction, the determination of the holocellulose content by acidification or the determination of the lignin content by acid hydrolysis is performed [4].

The total time for the extractive determination and the analysis of suberin content sums up to 44 hours at least. Therefore, it is based on a very long methodology with the use of different solvents and techniques that makes it difficult to implement it as a routine quality test in a cork manufacture.

The aims of the present study are the following: (i) identify faster and more sustainable methodologies for cork chemical composition testing, (ii) carry out extraction tests using alternative techniques, (iii) optimize an alternative methodology and (iv) validate the proposed methodology or sustainable methodologies.

GENERALITIES

New technologies have emerged that can be a potential tool to reduce the amount of solvent, treatment time and increase reproducibility, as well as energy consumption, thus improving the recovery of valuable compounds with lower costs for chemical analysis [8]. Methodologies based on newer technologies have been explored, such as microwave assisted extraction (MAE) or accelerated solvent extraction (ASE) system.

On one hand, MAE is a promising green extraction method based on electromagnetic radiation with a frequency of 0.3 to 300 GHz. The rapid energy supply is transformed by quickly heating the solvent and suspension. This treatment is homogeneous and efficient for extraction. MAE is based on the direct effect on molecules by ionic conduction dipole rotation. When MAE is applied, the absorption of energy in the plant matrix and especially by polar molecules such as

Verdum Virgos, M. Jové Martín, P

water (moisture content) leads to cell rupture that facilitates the recovery of molecules of interest. Furthermore, the increase in the extraction yield under microwave irradiation may be due to a synergistic combination of two transfer phenomena: mass and heat working in the same direction.

On the other hand, ASE is a sample preparation technique using solvents at elevated temperatures and pressures. Elevated temperature increases the efficiency of removal of analytes from the matrix. The increase in pressure keeps the solvent in a liquid state, even when the temperature is above the boiling point. It improves the diffusion of the analyte in it, making the extraction faster and more efficient. The ASE can be used to automate the process, mitigate variability, and ensure reproducible results.

Both technologies have been studied as alternatives to the Soxhlet methodology used for the determination of extractives in dichloromethane, ethanol and water, which are the first steps in the analysis of the chemical composition of cork (figure 2).

FIGURES



Figure 1. Cork chemical composition analysis diagram, sequential determination. Source ICSURO



Figure 2. Comparisons of classical extraction methodologies (soxhlet) with new alternatives: microwave assisted extraction (MAE) or accelerated solvent extraction (ASE) system (from left to right). Source ICSURO

REFERENCES

- Rives, J., Fernandez-Rodriguez, I., Gabarrell, X., & Rieradevall, J. (2012). Environmental analysis of cork granulate production in catalonia–northern spain. *Resources, conservation and recycling*, 2012, vol. 58, p. 132-142.
- [2] Pereira, Helena, ed. Cork: biology, production and uses. Elsevier, 2011.
- [3] Silva, S. P., Sabino, M. A., Fernandes, E. M., Correlo, V. M., Boesel, I. F., & Reis, R. L. Cork: properties, capabilities and applications. *International materials reviews*, 2005. vol. 50, no 6, p. 345-365.
- [4] Jové, P., Olivella, M. A., & Cano, L. Study of the variability in chemical composition of bark layers of Quercus suber L. from different production areas. *BioResources*, 2011, vol. 6, no 2, p. 1806-1815.
- [5] Conde, E., Cadahía, E., Garcia-Vallejo, M. C., & Gonźalez-Adrados, J. R. (1998). Chemical characterization of reproduction cork from spanish quercus suber. *Journal of*

Verdum Virgos, M. Jové Martín, P wood chemistry and technology, 1998, vol. 18, no 4, p. 447-469.

- [6] Pereira, H. Composição química da raspa em pranchas de cortiça de reprodução amadia. Boletim do Instituto dos Produtos Florestais-Cortiça, 1987, vol. 587, p. 231-233
- [7] Wise, L. E. (1946). Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. *Paper trade J*, 1946, vol. 122, p. 35-43.
- [8] Bouras, M., Chadni, M., Barba, F. J., Grimi, N., Bals, O., & Vorobiev, E. (2015). Optimization of microwave-assisted extraction of polyphenols from Quercus bark. *Industrial Crops and Products*, 2015, vol. 77, p. 590-601



EVALUATION OF 2,4,6-TRICHLOROANISOLE CONTAMINATION IN CORK OAK FORESTS WITH TWO DIFFERENT MANAGEMENT MODELS

F. Meloni*, M. Serra*, F. Pampiro*, M. Caredda† and M. Addis†

* Agris Sardegna Agenzia per la Ricerca in Agricoltura

Via Limbara 9, 07029 Tempio Pausania, Italy

e-mail: fmeloni@agrisricerca.it; maserra@agrisricerca.it; fpampiro@agrisricerca.it

[†] Agris Sardegna Agenzia per la Ricerca in Agricoltura 07100 Bonassai (SS), Italy e-mail: <u>mcaredda@agrisricerca.it; maddis@agrisricerca.it</u>

Keywords: Cork, TCA, forest, management, planks

Abstract. One of the major problems that affects the world of cork and consequently the wine industry is the well-known cork taint. 2,4,6-trichloroanisole (TCA) is considered the main contributor of this off-flavour, being the human perception threshold for this compound extremely low, in the order of a few ng $L^{-1}[1,2]$.

The project "TCA in foresta", funded by Regione Autonoma della Sardegna and developed by our research group of Agris Sardegna, aims to evaluate the concentration of TCA in raw planks, taking into account two models of cork forest management, one with undergrowth and one in which the undergrowth has been periodically removed for at least ten years. Four oak forests were selected in different locations, between the 350 and the 650 m of altitude above the sea level and, for each of them, the two models of management were considered. Moreover, in each area, the floristic composition, the tree-shrub situation and the phytosanitary status were evaluated in order to detect any correlations with the presence and the concentration of TCA. For each area, where all plants are almost the same age, 10 of these for bushy management and another ten for the hedge one were randomly chosen and extracted between July 2021 and July 2022. Each plank portion selected for the analysis, taken at mid-height, was in addition subjected



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

to a previous visual-qualitative test in order to find, in this case as well, possible correlations between the TCA concentration and the cork defects. In the 80 samples so far analysed, as regards the two different forms of management, significant differences were found. Nevertheless, this needs further confirmation as it is known that the strong localization of TCA in cork is a critical aspect [2] that will be investigated in more detail with a mapping of the entire planks. Concerning the correlations between the TCA concentration and the forest situation and the presence of defects (green cork, yellow stain, radical rot, etc.), at present no evident correlation has been found. Only in two cases, an abnormal concentration of TCA in association with the presence of radical rot, probably caused by Armillaria mellea, has been observed.

REFERENCES

- [1] H. R. Buser, C. Zanier, and H. Tanner, "Identification of 2,4,6-trichloroanisole as a potent compound causing cork taint in wine", J. Agric. Food Chem., vol. 30, pp. 359–362, 1982.
- [2] L. Cappellin, F. D. Lopez-Hilfiker, V. Pospisilova, L. Ciotti, P. Pastore, M. Gonin and M.
 A. Hutterli, "Thermal desorption-Vocus enables online nondestructive quantification of 2,4,6-trichloroanisole in cork stoppers below the perception threshold," Anal. Chem., vol. 92, pp. 9823–9829, 2020.

CORK FACADES: PERFORMANCE, ENVIRONMENTAL QUALITY AND PUBLIC PERCEPTION

João Athayde^{*1,2}, Iryna Skulska¹, Catarina Sequeira¹, and Conceição Colaço¹

* corresponding author, University of Lisbon, e-mail: joaoathayde07@gmail.com

¹Centre for Applied Ecology "Prof. Baeta Neves" (CEABN/InBIO), School of Agriculture, University of Lisbon, Tapada da Ajuda 1349-017 Lisbon, Portugal

²Center for Forestry Studies (CEF) School of Agriculture, University of Lisbon, Tapada da Ajuda 1349-017 Lisbon, Portugal

Keywords: sustainable buildings, environmental impact, citizen science, survey

Abstract.

Cork is an underrated material within architecture. It is a bio-based material with unique characteristics and advantages, such as thermal and acoustic insulation, fire resistance, and durability. Thus, this sustainable and renewable material is suitable for, among others, external cladding, internal lining, and insulation. Cork is also an environmentally friendly solution within building construction due to its low embodied energy consumption and low carbon footprint. Its light weight also makes it easier to transport and install than other materials used in architecture. Furthermore, cork can be easily customized with different colours and textures to create aesthetically pleasing façades and interiors.

The CORKinARCH project, funded by FCT, aims to raise public awareness on the use of this material and it production system, montado, in Portugal. The project is based on three main pillars of research: historical, social, and technological. The social part of the project, intends to assess, using a field questionnaire, the knowledge and perceptions of the general public and professionals about the material cork, the tree that it is the cork oak, and the importance of managing the ecosystem in which it grows.

Although the process of collecting information on public perception is under development, its first results indicate that: 1. Respondents have some ideas about the tree and the cork, together with the montados importance in Portugal; 2. Most of those interviewed are aware of the various uses of cork and agree that the use of this material in civil engineering can help to the buildings sustainability. However, there is a lack of knowledge about the types of building materials that can use cork.

The collection of information should be extended geographically, including other cities in Portugal.

João Athayde, Iryna Skulska, Catarina Sequeira and Conceição Colaço Furthermore, more detailed studies on the economics of cork-based building materials are recommended.

INTRODUCTION

The current trend towards constructing sustainable buildings and increasing awareness of the environment has led to a renewed interest in applying bio-architecture as an alternative construction method [1]. Furthermore, the EU has set the goal of having almost zero energy consumption in all new buildings by 2020 (Directive 2018/844/EU). Therefore, reducing buildings' energy intensity and environmental impact has become a top priority for EU development strategies and social objectives. Bio-based materials are promising for buildings in the 21st century due to their sustainability and versatility [1].

Cork is known worldwide as a bottle stopper, though it can have several other appliances, such as improving the thermal performance of buildings. This material meets the construction sector's requirements, combining lightness, elasticity and resilience, permeability, insulation, flame retardant qualities, and hypoallergenic properties [2,3].

In the last decades, cork has been used by Portuguese architects and designers for external cladding, such as in the pioneering work of Siza Vieira for the Expo2000 in Hannover. The Portuguese Pavilion was partially covered by pure agglomerated expanded cork and high-density cork sheets. The resilience and versatility of these non-timber forest products (NTFP) make them attractive for use in modern buildings, which can play an important role in reducing the environmental impact of the construction industry.

Cork is a cellular material with a very interesting set of physical, chemical, and biological properties and is one of the main NTFPs in the world. Many studies have been conducted on cork oak and cork, namely their growth, it structure, chemical composition, and properties [4,5,6,7]. However, despite research efforts and the current use of cork on building façades, there are no studies on the aging and response of these materials to weather and other biological phenomena.

GENERALITIES OF THE STUDY

The CORKinARCH project develops based on three objectives: 1. Studying the use of cork in the architecture of Alvaro Siza: concept and views on materials (focused on the study of archives donated by Alvaro Siza); 2. Examining cork products under various weather conditions and their aging characteristics to understand how environmental factors affect the performance of cork products; and 3. Analysis of public perception and spatial integration of cork in building construction.

The project's outreach work focuses on discovering, geolocating, and characterizing buildings with cork façades in Portugal. Information is collected using a web page designed to host the inventory obtained by the citizen science method. The same website disseminates information about cork, cork oak, the cork oak ecosystem and its associated biodiversity. In addition, a survey is being conducted to assess the knowledge and perceptions of the general public and specialists, particularly about cork, cork oak, and the importance of managing the ecosystem of cork oak forests.

João Athayde, Iryna Skulska, Catarina Sequeira and Conceição Colaço

Finally, it is designed to raise awareness among professionals about the environmental benefits of cork. To this end, it is planned to develop special training events within professional organizations. In addition, the transfer of knowledge acquired during the project will be presented as a guide on using cork in construction, aimed at architects and civil engineers, and the general public.

In general, the project is intended to carry out environmental activities to raise awareness and educate about cork in architecture. Since cork has a wide range of uses and cork oak is the Portuguese national tree, knowing and appreciating this specie is an important step towards its conservation.

METHODOLOGY AND PRELIMINARY RESULTS

At the Cork in Science and Application Congress (CSA) 2023, we intend to present the survey results that will be applied to residents of several Portuguese cities (Coimbra, Aveiro, Cascais, and Setúbal) with public buildings with cork exterior façades.

Until now, the survey was carried out between the 18th and 19th of March in Coimbra, at the Siza Vieira's Portuguese Pavilion. The location for collecting opinions from the general public was deliberately chosen to take advantage of the building model with exterior cork facades as an example.

During two days in this workplace, 71 people were interviewed, 56% males and 42% females. 2% of the respondents did not answer this question. As for the age groups of respondents, they were distributed evenly without statistically significant differences among the six groups defined, from 18 years old to over 65 years old. More than 80% of respondents were permanent residents of Coimbra, and only a small part were tourists or people with a temporary stay in this city.

The questions were divided into two main parts. The first part aimed to gather the respondents' opinions about the different materials used for cladding exterior façades and their level of satisfaction with the thermal and acoustic comfort of Portuguese buildings. The second part of the survey aimed to investigate the public perception of cork use in Portugal, including in civil construction.

Evaluation of building coatings in Portugal

The most mentioned building coatings materials during the survey were cement, stone, wood and Styrofoam (figure 1). Cork as a material for this kind of coating was mentioned by only 5% of the respondents.



Figure 1. A cloud of words that were collected during a survey about the most common material for façades in Portugal.

João Athayde, Iryna Skulska, Catarina Sequeira and Conceição Colaço

Among the various characteristics that an exterior facade of any building should have, the first three most mentioned were thermal and acoustic insulation (66% and 49% of responders), as well as impermeability (48%).

As for the thermal and acoustic comfort ratings of Portuguese buildings, most of the respondents were evaluated as having bad or very bad thermal and acoustic comfort (figure 2).

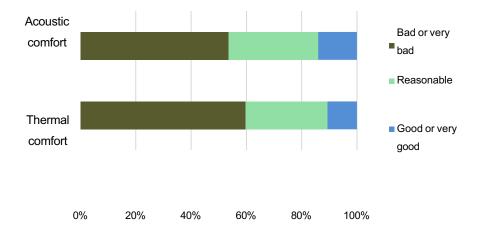


Figure 2. Results of respondents' assessment of thermal and acoustic comfort of buildings in Portugal.

Most of the respondents had experience building a house or at least renovating it. In the question regarding the preference of the materials country of production for exterior decoration of buildings, 96% of the respondents preferred to buy Portuguese materials. However, the decision on this purchase depended mostly on the price and quality of the product.

Public perception of cork and its usefulness

The results show that 83% of the respondents know what is the material cork and the tree from which it is extracted. In turn, 66% of respondents indicated the region with the highest abundance of montados in Portugal - Alentejo. In terms of the respondents' knowledge of the benefits of cork oak ecosystems, 66% believe that cork oaks contribute to biodiversity, 45% to a decreased risk of fires, 40% know it can conserve the soil and 37% that this specie is helping in the carbon sequestration.

As for questions directly related to cork as a raw material, 90% of respondents consider it sustainable, with important environmental and economic characteristics. Respondents demonstrated their knowledge of using cork for various purposes, such as the production of stoppers, footwear and clothing production, handicrafts, among others. However, 89% believe that the use of this material could be increased in the case of civil construction. This observation is also confirmed by the fact that, , according to respondents, the Siza Vieira's Portuguese Pavilion gains aesthetic and comfort characteristics because it uses cork on its facades.

DISCUTION AND CONCLUSIONS

Cork is a material with a wide range of applications and is now becoming increasingly popular due to its sustainable characteristics. It is derived from the bark of a cork oak tree, and understanding the cork oak ecosystem, montado, is essential if we want to use this resource sustainably.

Cork is becoming an increasingly popular material for civil construction due to its many advantages. Not only it is a sustainable material, but it also has excellent insulation, and acoustic and fire-resistant properties. This makes cork a suitable material for using in façades and other parts of the buildings.

Although most of the respondents in this study are aware of the benefits of this type of raw material and its origin, its use in Portugal is in its early stages of development, in what concerns civil engineering. It seems society is ready to introduce this material as an important element in the construction of buildings, but the barriers to this process remain unknown.

This study will be expanded geographically by conducting a similar survey in other populated cities in Portugal where it already exists a building with cork façades.

The collected information will serve as a basis for future research. For example, the economic direction seems to be interesting, namely the analysis of the availability of building materials based on cork, their price, the demand for this product, etc. Equally important is the research and innovation of cork-based building materials regarding their quality and versatility.

REFERENCES

[1] Sandak A., Sandak J., Brzezicki M., Kutnar A. Bio-based building skin.2019

[2] Pereira H. Cork: Biology, Production and Users. Elsevier BV (Eds.) Amsterdam 2007

[3] Fortes M.A., Rosa M.E., Pereira H.A. Cortiça. IST Press. Lisboa. 2004

[4] Graça J., Pereira, H. The periderm development in Quercus suber. IAWA Journal, 25:325-335. 2004

[5] Oliveira, V., Rosa, M.E., Pereira, H. Variability of the compression properties of cork. Wood Science and Technology, 48:937-948.

[6] Leite C., Pereira H., Cork-containing barks—a review. Frontiers in Materials 3, 63. 2016

[7] Knapic S., Oliveira V., Machado S., Pereira H. Cork as a building material: a review. European Journal of Wood and Wood Products, 74(6): 775-791. 2016



First A. Author, Second B. Author and Third C. Coauthor. 7-8 September 2023, Espinho, Portugal

REMEDIATION OF SOILS CONTAMINATED WITH PESTICIDES: SORPTION STUDIES OF LINDANE ONTO CORK

Paula V. Remor¹²³⁴, Julia Isidro⁴, Cristina Saez⁴, Manuel A.R. Rodrigo⁴, Sónia A. Figueiredo³ and Vítor J.P. Vilar¹²

¹Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM) Chemical Engineering Department, Faculty of Engineering, University of Porto Rua Dr. Roberto Frias, 4200-465 Porto, Portugal e-mail: up202010561@edu.fe.up.pt; vilar@fe.up.pt

> ²Associate Laboratory in Chemical Engineering (ALiCE) Faculty of Engineering, University of Porto Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

³REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto do Instituto Politécnico do Porto 4200-072 Porto, Portugal e-mail: saf@isep.ipp.pt

⁴Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies Universidad de Castilla La Mancha Campus Universitario, s/n 13071, Ciudad Real, Spain e-mail: Julia.Isidro@uclm.es; cristina.saez@uclm.es; Manuel.Rodrigo@uclm.es

Keywords: Regranulated cork, raw cork, pesticide, lindane, kinetics, equilibrium isotherm

Abstract. The contamination of soils and groundwater with lindane, a hazardous pesticide, has become a widespread problem for public health. Cork is a natural, renewable, and sustainable material, mainly used for wine stoppers production. Moreover, cork by-products can be used as sorbents for remediation purposes. This study examines the ability of two types of cork granules to sorb the pesticide lindane from liquid solutions, with the goal to used in permeable reactive barriers towards soil decontamination.

INTRODUCTION

Contamination of soils and groundwater by hazardous chemicals such as pesticides is a

First A. Author, Second B. Author and Third C. Coauthor.

widespread problem and a threat to public health. Lindane, an organochlorine pesticide, was widely used in the last decades because of its insecticide efficiency and is now a major source of unwanted by-products, present at many contaminated sites around the world. Thus, remediation techniques are needed to reduce the harmful effects caused by lindane contamination.

Cork, the outside bark of the cork oak tree (*Quercus suber* L.), 100% natural and sustainable material, is mainly used for wine stoppers production. A large amount of cork by-products is generated during cork stoppers production, which are used to produce cork/rubber composites, and agglomerates for wall and floor coverings. Recent studies demonstrate the potential of cork granules as a sustainable sorbent for oil spills clean up [1]. In this context, this work aims to study the sorption capacity of cork granules, with and without thermal treatment, for the uptake of the pesticide lindane from liquid solutions.

MATERIALS AND METHODS

Sorption studies were performed in batch to evaluate the capacity of cork to sorb the contaminant lindane. A lindane solution with a concentration of 3 mg L⁻¹ was prepared by dissolving a known weight of lindane in double de-ionized (Milli-Q) water.

Two types of cork byproducts, provided by Corticeira Amorim (Portugal), were used: raw cork (RAC) (1.0 - 2.0 mm) and regranulated cork (RGC) (1.0 - 2.0mm). The production of the RGC includes a pretreatment of the raw cork granules at high temperature (380°C), with water steam. RAC was washed twice in 2 h cycles with Milli-Q water at 60 °C. Before its use, both types of cork granules were dried in an oven at 60 °C overnight.

Experiments were conducted in 200 mL flasks containing 100 mL of lindane solution (3 mg L^{-1}) and cork granules (250, 500, 1000, and 2000 mg) at room temperature (25 °C), with constant agitation using a magnetic stirrer at 400 rpm. Samples were collected during the experiment and analysed for lindane concentration as described below, allowing the calculation of sorption capacity, the time needed to reach equilibrium, and also the equilibrium adsorption capacities, determined by mass balance to the batch reactor, according to Eq. 1.

$$V$$
(1)
$$q = \frac{V}{W}(C_0 - C_t)$$

Where *q* is the amount of lindane sorbed onto cork at time *t* per mass of cork (mg g⁻¹cork), *V* is the volume of solution (L), *W* is the mass of cork (g), C_0 and C_t is the concentration of lindane in the solution (mg L⁻¹) at t = 0 and t = t, respectively.

First A. Author, Second B. Author and Third C. Coauthor.

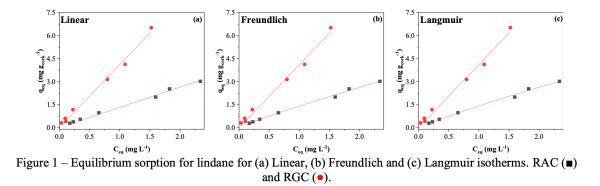
A liquid-liquid extraction was performed to extract the lindane from liquid samples. A 2 mL sample was mixed with 2 mL ethyl acetate, agitated for 5 minutes, then centrifuged for 10 minutes at 4000 rpm. The supernatant phase was analysed using a Gas Chromatography with an Electron Capture Detector (GC ECD).

RESULTS AND DISCUSSION

The lindane sorption isotherms were obtained for both types of cork granules (RAC and RGC) at room temperature (25 °C) (Fig. 1). Three isotherms models were fitted to the experimental data: the linear, the Freundlich and the Langmuir models, expressed by Eq. (2), (3) and (4), respectively.

$$q_{eq} = K_p C_{eq}$$
 (2) $q_{eq} = K_F C_{eq}^{\frac{1}{n}}$ (3) $q_{eq} = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}}$ (4)

Where q_{eq} is the amount of lindade at equilibrium in the solid phase (mg g⁻¹); K_p is the partition/affinity coefficient (L g⁻¹), K_F (mg^(1-1/n) L^{1/n} g⁻¹) and K_L (L mg⁻¹) are the Freundlich and the Langmuir coefficients, respectively, C_{eq} is the concentration of lindane at equilibrium in the liquid phase (mg g⁻¹), and *n* is the dimensionless parameter related to sorbate-sorbent affinity. Figure 1 presents the fitting of the three isotherms models to the equilibrium data for both cork granules.



The three models were able to fit the experimental equilibrium data without any statistical difference. Since *n* is close to 1, it can be assumed that the main mechanism of sorption is partitioning, and that K_F is an approach to a sorption partition coefficient (K_p).

Model	Cork	Parameter		R ²	$S_{R}^{2} (mg g^{-1})^{2}$	Cork	Parameter		R ²	$S_{R}^{2} (mg g^{-1})^{2}$
Linear	RGC	K_p	(41±1)×10 ⁻¹	0.995	3.5×10 ⁻¹	RAC	K_p	(132±3)×10 ⁻²	0.996	6.4×10 ⁻²
Langmuir		K_L	(1±0.1)×10 ⁻³	0.987	3.5×10 ⁻¹		K_L	(8±3)×10 ⁻²	0.993	4.3×10 ⁻²
		q_m	$(4\pm0.4)\times10^{1}$				q_m	$(2\pm0.9)\times10^{1}$		
Freundlich		K_F	(41±1)×10 ⁻¹	0.987	3.5×10 ⁻¹		K_F	(141±4)×10 ⁻²		3.5×10 ⁻²
		n	(99±9)×10 ⁻²				n	(111±5)×10 ⁻²		

Table 1 – Estimated parameters for the equilibrium models (value±standard deviation). Residual sum of square (S_R^2) and coefficient of determination (R^2) .

Batch sorption studies showed faster kinetics when increasing the cork mass, since a higher number of active sites are available for lindane uptake. RGC shows a superior affinity towards lindane than RAC. This is mainly associated with the higher hydrophobicity of RGC, matching the hydrophobic characteristic of the lindane.

Two mass transfer models (Eqs. 5 and 6) were developed to predict the lindane uptake kinetics by cork granules, considering the following assumptions: i) isothermal process; ii) spherical particles and iii) linear partitioning equilibrium model. Model 1 (Eq. 5) considers the formation of an external sublayer around the cork particles, in which the lindane molecules diffuse from the bulk fluid to the surface of the particles, while Model 2 (Eq. 6) considers the particle's diffusion (linear driving force model).

$$q = \frac{K_p C_{b_0}}{1 + \xi_m} \left\{ 1 - e^{\left[- \left(\frac{1 + \xi_m}{\xi_m}\right) \frac{t}{\tau_f} \right]} \right\} ; \xi_m = \frac{W}{V} K_p ; \tau_f = \left(\frac{\varepsilon_b}{1 - \varepsilon_b}\right) \frac{1}{k_f a_p} ; a_p = \frac{3}{r_p}$$
(5)

$$q = \frac{K_p C_{b_0}}{1 + \xi_m} \left[1 - e^{-k_p a_p (1 + \xi_m) t} \right]; \ \xi_m = \frac{W}{V} K_p \ ; \ k_p a_p = \frac{15}{\tau_d}; \ \tau_d = \frac{R^2}{D_h}$$
(6)

Where $q \pmod{g^{-1}}$ is the amount of lindane sorbed at time t (s), G_0 is the initial concentration

First A. Author, Second B. Author and Third C. Coauthor.

of lindane in the bulk (mg L⁻¹), ξ_m is the batch mass capacity factor, τ_f is the time constant for lindane diffusion in the film (s), ε_b is the bulk porosity, k_f is the film mass transfer coefficient (cm s⁻¹), a_p is the external surface area per unit particle volume (cm² cm⁻³), r_p is the particle radius (cm), τd is the time constant for lindane diffusion in the particle, kp is the mass transfer coefficient for interparticle diffusion (cm s-1) and *Dh* is the coefficient of homogeneous diffusion in the particle. A cork density of 540 g L⁻¹ and a particle radius of 0.15 cm were

assumed. The initial lindane concentration was 3.1 mg L⁻¹. Both models adequately predicts the experimental data and presented a very similar

behaviour (Fig. 2) for both type of cork granules.

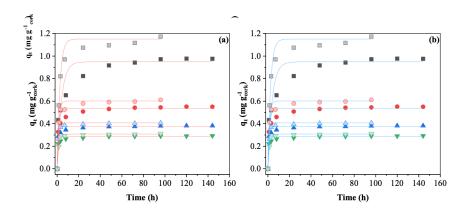


Figure 2 – Kinetic studies for RAC (solid symbols) and RGC (open sym bols): (a) Model 1 (red lines) and (b) Model 2 (blue lines), for different cork weights. 250 mg (); 500 mg (); 1000 mg (); 2000 mg ().

As reported above, faster sorption kinetics (lower τ_f and τ_d) are obtained for higher solid/liquid ratios, due to higher amount of binding sites available for lindane uptake (Table 2). Since the porosity of cork granules consists almost exclusively of external macropores (internal cells are closed), intraparticle diffusion can be considered negligible and the main resistance to lindane diffusion is in the particle film side. Regarding the resistance to diffusion in the film (k_f), values are in the same order of magnitude, since it only depends on the stirring velocity of the suspension.

First A. Author, Second B. Author and Third C. Coauthor.

Parameter	Model		RC	GC		RAC				
		250 mg	500 mg	1000 mg	2000 mg	250 mg	500 mg	1000 mg	2000 mg	
$\tau_f(s)$		$(30\pm3)\times10^{1}$	$(17\pm2)\times10^{1}$	167±9	171±8	$(4\pm1)\times10^{2}$	(17±3)×10 ¹	(9±1)×10 ¹	(9±1)×10 ¹	
\mathbb{R}^2	1 (Eq.5)	0.977	0.979	0.995	0.996	0.897	0.944	0.972	0.969	
$S_R^2 (mg g^{-1})^2$		3.6×10 ⁻³	8.8×10 ⁻⁴	9.9×10 ⁻⁵	4.4×10 ⁻⁵	1.4×10 ⁻²	2.1×10-3	4.9×10 ⁻⁴	3.1×10 ⁻⁴	
$k_f \times 10^{-3} (\text{cm s}^{-1})$		36±4	32±4	21±1	15.8±0.8	23±5	32±6	41±6	31±5	
τ_d (s)		$(25\pm2)\times10^{3}$	(27±3)×10 ³	(40±2)×10 ³	(54±3)×10 ³	(15±3)×10 ³	$(10\pm 2)\times 10^3$	(7±1)×10 ³	(9±1)×10 ³	
R ²	2 (Eq.6)	0.977	0.978	0.995	0.996	0.897	0.944	0.972	0.969	
$S_R^2 (mg g^{-1})^2$		3.6×10 ⁻³	8.8×10 ⁻⁴	9.9×10 ⁻⁵	4.4×10 ⁻⁵	1.4×10 ⁻²	2.1×10-3	4.9×10 ⁻⁴	3.1×10 ⁻⁴	
$D_h (cm^2/s)$		9×10 ⁻⁷	8×10 ⁻⁷	6×10 ⁻⁷	4×10 ⁻⁷	1×10 ⁻⁶	2×10 ⁻⁶	3×10 ⁻⁶	2×10 ⁻⁶	

Table 2 – Estimated parameters for the mass transfer model (value±standard deviation). Residual sum of square (S_R^2) and coefficient of determination (R^2) .

CONCLUSIONS

Cork granules, a byproduct of the cork industry, showed promising results for the uptake of lindane from liquid solutions. The RGC granules presented higher affinity to lindane than RAC. A faster sorption kinetics were obtained for higher solid/liquid ratios.

REFERENCES

[1] R. S. Souza, P. S.S. Porto, A. M.A. Pintor, G. Ruphuy, M. F. Costa, R. A.R. Boaventura, and V. J.P. Vilar. "New Insights on the Removal of Mineral Oil from Oil-in-Water Emulsions Using Cork by-Products: Effect of Salt and Surfactants Content." Chemical Engineering Journal, 285: 709–17, 2016.



THERMAL ANISOTROPY OF NATURAL CORK

T. Santos*, †, ‡, J. S. Amaral†, V. S. Amaral† and V. A. F. Costa*

* University of Aveiro
 TEMA – Centre for Mechanical Technology and Automation
 Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
 e-mail: <u>tiago.santos@ua.pt</u>, e-mail: <u>v.costa@ua.pt</u>

[†] University of Aveiro CICECO – Aveiro Instituto of Materials Physics Department Campus Universitário de Santiago, 3810-193 Aveiro, Portugal e-mail: jamaral@ua.pt, e-mail: vamaral@ua.pt

[‡] Polytechnic of Leiria CDRSP – Centre for Rapid and Sustainable Product Development Rua de Portugal – Zona Industrial, 2430-028 Marinha Grande, Portugal e-mail: tiago.a.santos@ipleiria.pt

Keywords: Natural cork, thermal anisotropy, thermal diffusivity, infrared thermography

Abstract. The present work aims to study the thermal anisotropy of natural cork. Plane slice samples with 1.4 mm average thickness were cut for that purpose along the principal radial, longitudinal and tangential directions from a bark previously treated for cork stoppers production. Samples were heated on the rear face using a copper needle coupled to a Peltier element. An in-plane thermographic technique was implemented to study the space-time temperature evolution in the samples' front surfaces. Temperature measurements were made using a Flir SC5650 infrared camera. Measurements of thermal diffusivity in the three principal directions were performed, and the natural cork thermal anisotropy evaluated. The implemented technique allows in-plane thermal diffusivity direct measurements, and post evaluation of the

T. Santos, J. S. Amaral, V. S. Amaral and V. A. F. Costa.

natural cork thermal anisotropy. Even if presenting some expected variability, as cork is a natural product, results of the measured thermal diffusivities are compared with the results available in the literature. Thermal diffusivities from 0.15 mm²/s and 0.14 mm²/s along radial and non-radial directions were obtained, within the average values range of 0.08 mm²/s up to 0.24 mm²/s found in the literature. The thermal diffusivity along the radial direction was found to be 10% higher than along the non-radial directions, evidencing the natural cork thermal diffusivity and conductivity anisotropies. This gives useful information on the difference between the average thermal properties of natural cork, and on how they depend on the orientation of the cork elements on the original cork bark.

INTRODUCTION

Cork is a natural material with important and interesting properties, with many current and potential uses, namely as thermal insulator, noise and shock absorber, flame retarder, wine stopper, flexible joints and several components, etc. [1-2]. Cork can be used as natural cork, as extracted from the cork bark, or as agglomerated cork (granulated cork agglomerated using some kind of resin as a binder). Given the cork natural character, its properties cannot be accurately reproduced, even if some patterns can be identified, its properties presenting some variability. Due to its cellular nature, and to its natural development and growth as the shell of the quercus suber tree, cork presents anisotropy, with different properties along different directions, such as the water diffusion coefficient and the cork-cork friction coefficient, which are 40 times higher in non-radial directions and ~1.3 times higher in the radial direction, respectively [1,2]. For the same reasons, it is also expected to observe the thermal anisotropy of the natural cork, which affects its thermal diffusivity and thermal conductivity. This work aims to experimentally evaluate the thermal anisotropy of natural cork using infrared thermography. This technique allows the visualization of the space-time thermal evolution on the samples surface, and the determination of the heat wave propagation along the principal directions of thin plate-like materials.

THERMAL DIFFUSIVITY MEASUREMENTS

Considering a sample with the form of an infinite plate of thickness d which is instantaneously heated on the rear face by a circular Gaussian heat source of radius R, if the heat losses are neglected, the temperature distribution on the front face can be expressed as a Gaussian [3].

T. Santos, J. S. Amaral, V. S. Amaral and V. A. F. Costa.

$$T(r, z, \tau) = \beta \cdot e^{-\frac{2r^2}{C^2}}; \ c^2 = R^2 + 8\alpha\tau$$
(1)

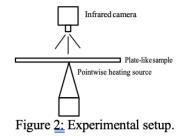
where α is the thermal diffusivity and $\mathcal{B} \propto (Q, R, d, t)$, an expression that accounts for the total heat, Q, supplied from the beginning of heating up to instant τ , and thickness d. R is defined as the distance from the pointwise heat source where the beam intensity decreases its intensity by a factor of $1/e^2$, and r is the radial coordinate (measured away from the pointwise heat source). Once known the space-time temperature distribution of the front face, a Gaussian fit for each time instant τ allows obtaining the effective width (c) as a function of time, from which the thermal diffusivity α along any given direction can be obtained. The described procedure is valid for instants of elapsed time τ , for which the heat wave is far from reaching the edges of the plate-like sample. In the present study, we focus on the ratios of the thermal properties (thermal diffusivity and thermal conductivity) along the principal (radial, longitudinal and tangential) directions, rather than on their absolute values.

Three thin plate-like samples with an approximate thickness of 1.4 mm were obtained from a bark piece. The thickness of each sample develops along one of the (radial, longitudinal and tangential) principal directions, as schematically represented in Fig. 1. The thickness of each sample develops along one of the principal directions, orthogonally to the plane defined by the other two principal directions where the heat diffusion is evaluated.

Heating was imposed on the rear face of the samples through a needle-like copper heater, its base being heated using a Peltier heater as illustrated in Fig. 2. In this way, heating is approximated as much as possible to a point source heating on the rear face of the plate-like thin samples. A FLIR SC5650 thermographic camera was used for temperature mapping of the samples' front surfaces, as a function of time.



Figure 1: Schematic of the radial (*r*), longitudinal (*l*) and tangential (*t*) principal directions.



RESULTS

Figure 3 depicts the pair (c^2, τ) linearity, which accordingly to eq. (1) allows the evaluation of the sample thermal diffusivities along the direction of interest. Insets show the cork platelike sample (a), the infrared image (b) and the respective temperature profiles along the radial and tangential directions (c), 22 s after starting heating.

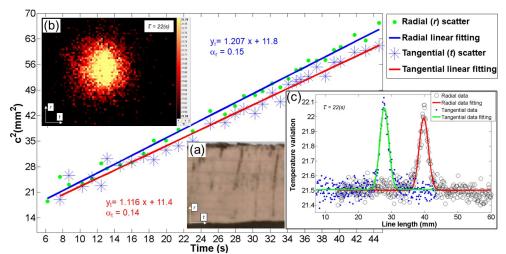


Figure 3: Thermal diffusivities evaluation in the radial – tangential directions. Insets: (a) cork plate-like sample; (b) infrared thermal image; (c) temperature profiles data and Gaussian fitting along *l* and *t* directions for $\tau = 22$ s.

Table 1 summarizes the thermal diffusivity measurements along the principal directions, considering (1) the radial – longitudinal (r-l) surface, (2) the radial – tangential (r-t) surface, and (3) the longitudinal – tangential (l-t) surface. In addition to the thermal diffusivity, Table 1 includes also the respective ratios for each of the considered surfaces and the calculated heat source radius *R*. The relative errors for α was determined below 2% for all directions.

		Tangen	ntial (t)	Longitud	inal (<i>l</i>)	Radia		
Orienta	tion/surface	$\alpha (mm^2/s)$	R (mm)	$\alpha (mm^2/s)$	R (mm)	$\alpha (mm^2/s)$	R (mm)	α's ratios
(1)	r-l			0.138	1.8	0.155	1.7	1.13
(2)	r-t	0.140	1.8			0.151	1.9	1.08
(3)	l-t	0.097	1.9	0.111	1.8			1.15

Table 1 : Thermal diffusivity analysis along the different principal r, t and l directions.

SUMMARY

As cork is a natural product its properties present some variability. Silva et al. [1] refer that cork density can vary between 120 kg/m³ and 180 kg/m³ for amadia, and between 160 kg/m³ and 240 kg/m³ for virgin cork. Average values from 0.08 mm²/s [4] up to 0.24 mm²/s [5] are found in the literature for thermal diffusivity. Values of 0.003 mm²/s [6] and 1 mm²/s [2] are also reported, differing from the generality of the literature in one order of magnitude. These discrepancies evidence a need for clarification and confirmation. The thermal diffusivities of approximately 0.15 mm²/s and 0.14 mm²/s along the radial and non-radial principal directions measured in the present work reflect the cork natural development and growth [1,2]. Thermal diffusivity is approximately 10% higher along the principal radial direction than along the non-radial (longitudinal and tangential) principal directions.

ACKNOWLEDGEMENTS

Authors acknowledge the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by the FCT/MEC (PIDDAC) and by the projects UIDB/00481/2020 and UIDP/00481/2020, FCT and CENTRO-01-0145-FEDER-022083, Centro2020, under the PORTUGAL 2020 Partnership Agreement.

REFERENCES

 Silva, S.P.; Sabino, M.A.; Fernandes, E.M.; Correlo, V.M.; Boesel, L.F.; Reis, R.L. "Cork : Properties, Capabilities and Applications". Int. Mat. Rev., Vol.50, no.6, pp. 345–366, 2005. T. Santos, J. S. Amaral, V. S. Amaral and V. A. F. Costa.

- [2] Gil, L. Cortiça: Produção, Tecnologia e Aplicação; (INEGI), I.N. de E. e T.I., Ed.; Gráfica Rosial, Lda.: Lisbon, 1998.
- [3] Cernuschi F., Russo, A., Lorenzoni, L., "In-plane Thermal Diffusivity Evaluation by Infrared Thermography", Rev. Scient. Inst., Vol.72, no.10, pp. 3988–3995, 2001.
- [4] Barreca, F.; Fichera, C.R. Thermal Insulation Performance Assessment of Agglomerated Cork Boards, 2015.
- [5] Agglomerated Black Cork Thermoacoustic Insulation La Sureda Cork Available online: https://lasureda-cork.com/en/ecological-cork.html (accessed on 25 Fev. 2022).
- [6] Thermal Conductivity of Cork Insulation Available online: https://www.nuclearpower.com/nuclear-engineering/heat-transfer/heat-losses/insulation-materials/thermalconductivity-of-cork-insulation/ (accessed on 25 Fev. 2022).



INSIGHTS INTO CORK WEATHERING REGARDING COLOUR, CHEMICAL AND CELLULAR CHANGES

Isabel Miranda*, Ana Lourenço, João Atayde and Helena Pereira

Forest Research Center and Associated Laboratory TERRA, School of Agriculture, University of Lisbon, Tapada da Ajuda, 1349-017 Lisboa, Portugal <u>https://www.isa.ulisboa.pt/cef/</u> https://www.isa.ulisboa.pt/cef/laboratorio-associado-terra/

e-mail: <u>imiranda@isa.ulisboa.pt</u>, <u>analourenco@isa.ulisboa.pt</u>, <u>joaoathayde07@gmail.com</u>, <u>hpereira@isa.ulisboa.pt</u>

Keywords: Cork, Weathering, Biodegradation, Colour, FTIR

Abstract. Knowledge on cork weathering is important for cork applications in outdoor environments namely as surfacing material in building facades. Colour changes have the highest visual impact but impact at cellular and chemical levels may also be relevant. This study presents a first analysis of weathering of cork regarding impact on colour, chemical composition and structure of natural cork. The effect of temperature (40°C and 60°C) in closed environments and outdoor field testing with samples inserted in and above ground were followed during one year. Measurements of colour parameters were made and cellular observations with scanning electron microscopy and chemical features were analysed by FTIR. These are preliminary results with the project CorkinARCH- Cork facades: performance, environmental quality and public perception.

INTRODUCTION

Cork, a cellular material with a very interesting set of physical, biological and chemical properties, has been extensively studied in relation to structure, chemical composition and properties ^[1]. Despite these research efforts, there are no studies focusing on cork weathering, namely on the impact of light, and especially UV, humidity and rain as well as of polluted environments, e.g. urbans spaces, and soil contact on cork materials. These aspects are important since cork products may be applied in outdoor environments as surfacing and insulation materials. The use of cork in facades has increased in the last years following some highlighted buildings with outdoor surfacing with cork, e.g. in the Hannover and Shanghai World Exhibitions.

The properties of cork depend on the chemical features of its structural components that are located on the faces and edges of the cells, forming a three-dimensional network of a solid matrix that surrounds the air-filled cells. The properties of cork, including its chemical and biological inertness and durability, are directly related to its chemical and cellular composition ^[2].

EXPERIMENTAL DESIGN AND RESULTS

Cork sheets with approximately 1cm thickness were cut tangentially from thin cork planks provided by Indústria Amorim. The tested samples were cut from these sheets and the observations were made on their tangential sections. Two series of tests were carried out:

- i) Impact of temperature in closed environments: Square samples of approximately 10x10 cm2 were used and placed in drying chambers at 40°C and 60°C
- Outdoor field tests: Rectangular samples of approximately 10x30 cm² were used and placed in a biodegradation field test buried in the soil at approximately mid-length, following the procedures of biodegradation testing in natural open-air burial conditions set in ASTM G160–12^[3].

The tests started January 2022, and results will be presented for the first 12 months. The measurements include the colour of each sample using the CIELAB methodology and chemical characterization by FTIR-ATR. Scanning electron microscopy (SEM) was used for observations of the cellular structure. In the case of the buried samples, observations were made on the buried part and on the air-exposed part.

The observed changes – at colour, chemical and cellular levels – will be presented and discussed.

REFERENCES

- [1] H. Pereira, "Cork: Biology, Production and Uses". Elsevier, Amsterdam. 2007.
- [2] H. Pereira, "The rationale behind cork properties: A Review of structure and chemistry", BioResources, 10(3): 213-218, 2015.
- [3] ASTM G160–12 Standard Practice for Evaluating Microbial Susceptibility of Nonmetallic Materials by Laboratory Soil Burial; ASTM International: West Conshohocken, PA, USA, 2019.



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal 7-8 September 2023, Espinho, Portugal

PROMOTING THE DEVELOPMENT OF BLIND AND VISUALLY IMPAIRED CHILDREN THROUGH A CORK TOY

Ana Rita Ferreira*, Eduardo Noronha*, Ricardo Sousa† and Gabriel Serra†

* University of Aveiro
 ID+ - Research Institute for Design, Media and Culture
 Campus Santiago, 3810-193 Aveiro, Portugal
 e-mail: <u>anarita.ferreira@ua.pt</u>
 e-mail: <u>eduardonoronha@ua.pt</u>

[†] University of Aveiro TEMA - Centre for Mechanical Technology and Automation Campus Santiago, 3810-193 Aveiro, Portugal e-mail: <u>rsousa@ua.pt</u> e-mail : <u>gfserra92@ua.pt</u>

Keywords: Blindness, visual impairment, design children toy, cork

Abstract. The term blindness refers to a wide range of visual impairments [1]. According to the World Health Organization, there were approximately 2.2 billion visually impaired people in 2019 [2]. In the following year, data pointed to about 75 million blind people, including 1.4 million children [3].

Since the moment of birth, vision is a crucial tool for learning about the world as it is the most dominant sense [2], [4]. Vision also improves children's motivation and increases their curiosity to explore [4]. Although the developmental processes of sighted and visually impaired children are similar, the latter face development difficulties and delays [5]. For example, blind children often learn to crawl and walk later and are less confident to move around because visual information is especially important for obtaining balance and posture [6], [7].

There are available on the market mobility devices that aim to compensate for the lack of motor coordination of visually impaired and blind infants [7]. However, these products are



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

only usable by toddlers who are already able to stand and walk. There is a need for products that can help these children develop autonomous movement skills as early as possible. This paper describes the development process of the Rall Toy that promotes innovation by taking advantage of cork's benefits to encourage blind children's development through motor, cognitive and sensorial stimulation. The project was born in an academic context and its final goal is to bring joy to all children, but with special attention to the early needs of blind infants. It is designed to encourage babies' first movements and to increase their self-confidence and independence. The toy is a play carpet on which children can build a ramp using two types of modular blocks in a Lego-like construction logic and play with noisy balls that make different sounds depending on the objects inside. There is also a toy car on the carpet with a predetermined path to help children reach the end of the ramp so they can pick up the balls, bring them back and play again. This toy uses the sounds of the balls and the properties of the composite cork agglomerates to trigger auditory and tactile sensations to keep children motivated.

REFERENCES

- CNIB FOUNDATION, "What is Blindness?," 2022. https://www.cnib.ca/en/sight-lossinfo/blindness/what-blindness?region=on (accessed Mar. 22, 2023).
- [2] World Health Organization, "World report on vision," 2019.
- [3] CUF, "Cegueira: o que é, sintomas e tratamento | CUF," 2020. https://www.cuf.pt/saude-a-z/cegueira (accessed Mar. 17, 2023).
- [4] RNIB, "Information about vision impairment Guide for parents." 2016.
- [5] Safe Toddles, Learning from Lily: Growing up Mobility Visually Impaired, (2020).
 Accessed: Jan. 05, 2023. [Online Video]. Available: https://www.youtube.com/watch?v=BijN08w0JzA&ab channel=SafeToddles
- [6] RNIB, "Effective Practice Guide Learning through play in the early years." 2020.
- [7] N. A. G. Z. Evyapan, "EXPERIENCING SPACE WITHOUT VISION," 1997.



PIEZORESISTIVE SENSORS SYNTHESIZED DIRECTLY ON CORK

Alexandre F. Carvalho*, Ana. M, Rodrigues*, António J. S. Fernandes* and Florinda M. Costa*

* i3N and Physics Department
 University of Aveiro
 Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
 e-mail: <u>alexandre.carvalho@ua.pt</u>

Keywords: Laser-processing, Graphene, Cork, Sensors

Abstract.

We are living in the era of the Internet of Things (IoT), where the ability to sensorize materials and create devices capable of detecting changes in our bodies assumes a significant role. In recent times, the capability to detect small physical/chemical changes has grown due to advancements in manipulating materials at a previously difficult-to-achieve scale. Among the many possible technologies, laser processing stands out for its ability to modify the surface of materials while preserving their intrinsic properties. This also applies to cork, as its interaction with a laser beam may result in the formation of a Laser-induced Graphene (LIG) foam, providing conductive properties that enable the direct scribing of pressure sensors [1]. This process enabled the development of sensors capable of monitoring human gait through the analysis of pressure signals from distinct foot regions. The conductive regions formed by graphene sheets exhibit sheet-resistances of less than 100 Ω sq⁻¹, demonstrate piezoresistive response up to 1132 kPa, and sensitivities of up to 0.02 kPa⁻¹. Different strategies have also been explored to improve the long-term operation of these sensors.



REFERENCES

CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

[1] A. F. Carvalho, A. J. S. Fernandes, R. Martins, E. Fortunato, F. M. Costa, "Laser-induced graphene piezoresistive sensors synthetized directly on cork insoles for gait analysis" Adv. Mater. Technol., no. 2000630, pp.1–8, 2020.

CORK FACADES: PERFORMANCE, ENVIRONMENTAL QUALITY AND PUBLIC PERCEPTION

João Athayde^{*1,2}, Iryna Skulska¹, Catarina Sequeira¹, and Conceição Colaço¹

* corresponding author, University of Lisbon, e-mail: joaoathayde07@gmail.com

¹Centre for Applied Ecology "Prof. Baeta Neves" (CEABN/InBIO), School of Agriculture, University of Lisbon, Tapada da Ajuda 1349-017 Lisbon, Portugal

²Center for Forestry Studies (CEF) School of Agriculture, University of Lisbon, Tapada da Ajuda 1349-017 Lisbon, Portugal

Keywords: sustainable buildings, environmental impact, citizen science, survey

Abstract.

Cork is an underrated material within architecture. It is a bio-based material with unique characteristics and advantages, such as thermal and acoustic insulation, fire resistance, and durability. Thus, this sustainable and renewable material is suitable for, among others, external cladding, internal lining, and insulation. Cork is also an environmentally friendly solution within building construction due to its low embodied energy consumption and low carbon footprint. Its light weight also makes it easier to transport and install than other materials used in architecture. Furthermore, cork can be easily customized with different colours and textures to create aesthetically pleasing façades and interiors.

The CORKinARCH project, funded by FCT, aims to raise public awareness on the use of this material and it production system, montado, in Portugal. The project is based on three main pillars of research: historical, social, and technological. The social part of the project, intends to assess, using a field questionnaire, the knowledge and perceptions of the general public and professionals about the material cork, the tree that it is the cork oak, and the importance of managing the ecosystem in which it grows.

Although the process of collecting information on public perception is under development, its first results indicate that: 1. Respondents have some ideas about the tree and the cork, together with the montados importance in Portugal; 2. Most of those interviewed are aware of the various uses of cork and agree that the use of this material in civil engineering can help to the buildings sustainability. However, there is a lack of knowledge about the types of building materials that can use cork.

The collection of information should be extended geographically, including other cities in Portugal. Furthermore, more detailed studies on the economics of cork-based building materials are recommended.

João Athayde, Iryna Skulska, Catarina Sequeira and Conceição Colaço INTRODUCTION

The current trend towards constructing sustainable buildings and increasing awareness of the environment has led to a renewed interest in applying bio-architecture as an alternative construction method [1]. Furthermore, the EU has set the goal of having almost zero energy consumption in all new buildings by 2020 (Directive 2018/844/EU). Therefore, reducing buildings' energy intensity and environmental impact has become a top priority for EU development strategies and social objectives. Bio-based materials are promising for buildings in the 21st century due to their sustainability and versatility [1].

Cork is known worldwide as a bottle stopper, though it can have several other appliances, such as improving the thermal performance of buildings. This material meets the construction sector's requirements, combining

lightness, elasticity and resilience, permeability, insulation, flame retardant qualities, and hypoallergenic properties [2,3].

In the last decades, cork has been used by Portuguese architects and designers for external cladding, such as in the pioneering work of Siza Vieira for the Expo2000 in Hannover. The Portuguese Pavilion was partially covered by pure agglomerated expanded cork and high-density cork sheets. The resilience and versatility of these non-timber forest products (NTFP) make them attractive for use in modern buildings, which can play an important role in reducing the environmental impact of the construction industry.

Cork is a cellular material with a very interesting set of physical, chemical, and biological properties and is one of the main NTFPs in the world. Many studies have been conducted on cork oak and cork, namely their growth, it structure, chemical composition, and properties [4,5,6,7]. However, despite research efforts and the current use of cork on building façades, there are no studies on the aging and response of these materials to weather and other biological phenomena.

GENERALITIES OF THE STUDY

The CORKinARCH project develops based on three objectives: 1. Studying the use of cork in the architecture of Alvaro Siza: concept and views on materials (focused on the study of archives donated by Alvaro Siza); 2. Examining cork products under various weather conditions and their aging characteristics to understand how environmental factors affect the performance of cork products; and 3. Analysis of public perception and spatial integration of cork in building construction.

The project's outreach work focuses on discovering, geolocating, and characterizing buildings with cork façades in Portugal. Information is collected using a web page designed to host the inventory obtained by the citizen science method. The same website disseminates information about cork, cork oak, the cork oak ecosystem and its associated biodiversity. In addition, a survey is being conducted to assess the knowledge and perceptions of the general public and specialists, particularly about cork, cork oak, and the importance of managing the ecosystem of cork oak forests.

Finally, it is designed to raise awareness among professionals about the environmental benefits of cork. To this end, it is planned to develop special training events within professional organizations. In addition, the transfer of knowledge acquired during the project will be presented as a guide on using cork in construction, aimed at architects and civil engineers, and the general public. In general, the project is intended to carry out environmental activities to raise awareness and educate about cork in architecture. Since cork has a wide range of uses and cork oak is the Portuguese national tree, knowing and appreciating this specie is an important step towards its conservation.

METHODOLOGY AND PRELIMINARY RESULTS

At the Cork in Science and Application Congress (CSA) 2023, we intend to present the survey results that will be applied to residents of several Portuguese cities (Coimbra, Aveiro, Cascais, and Setúbal) with public buildings with cork exterior façades.

Until now, the survey was carried out between the 18th and 19th of March in Coimbra, at the Siza Vieira's Portuguese Pavilion. The location for collecting opinions from the general public was deliberately chosen to take advantage of the building model with exterior cork facades as an example.

During two days in this workplace, 71 people were interviewed, 56% males and 42% females. 2% of the respondents did not answer this question. As for the age groups of respondents, they were distributed evenly without statistically significant differences among the six groups defined, from 18 years old to over 65 years old. More than 80% of respondents were permanent residents of Coimbra, and only a small part were tourists or people with a temporary stay in this city.

The questions were divided into two main parts. The first part aimed to gather the respondents' opinions about the different materials used for cladding exterior façades and their level of satisfaction with the thermal and acoustic comfort of Portuguese buildings. The second part of the survey aimed to investigate the public perception of cork use in Portugal, including in civil construction.

Evaluation of building coatings in Portugal

The most mentioned building coatings materials during the survey were cement, stone, wood and Styrofoam (figure 1). Cork as a material for this kind of coating was mentioned by only 5% of the respondents.

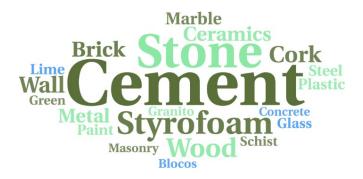


Figure 1. A cloud of words that were collected during a survey about the most common material for façades in Portugal.

João Athayde, Iryna Skulska, Catarina Sequeira and Conceição Colaço

Among the various characteristics that an exterior facade of any building should have, the first three most mentioned were thermal and acoustic insulation (66% and 49% of responders), as well as impermeability (48%). As for the thermal and acoustic comfort ratings of Portuguese buildings, most of the respondents were

evaluated as having bad or very bad thermal and acoustic comfort (figure 2).

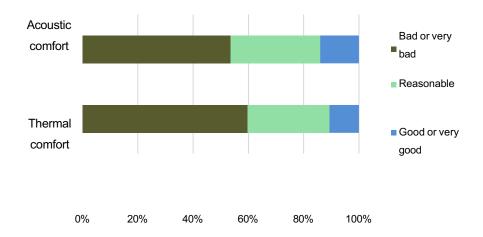


Figure 2. Results of respondents' assessment of thermal and acoustic comfort of buildings in Portugal.

Most of the respondents had experience building a house or at least renovating it. In the question regarding the preference of the materials country of production for exterior decoration of buildings, 96% of the respondents preferred to buy Portuguese materials. However, the decision on this purchase depended mostly on the price and quality of the product.

Public perception of cork and its usefulness

The results show that 83% of the respondents know what is the material cork and the tree from which it is extracted. In turn, 66% of respondents indicated the region with the highest abundance of montados in Portugal - Alentejo. In terms of the respondents' knowledge of the benefits of cork oak ecosystems, 66% believe that cork oaks contribute to biodiversity, 45% to a decreased risk of fires, 40% know it can conserve the soil and 37% that this specie is helping in the carbon sequestration.

As for questions directly related to cork as a raw material, 90% of respondents consider it sustainable, with important environmental and economic characteristics. Respondents demonstrated their knowledge of using cork for various purposes, such as the production of stoppers, footwear and clothing production, handicrafts, among others. However, 89% believe that the use of this material could be increased in the case of civil construction. This observation is also confirmed by the fact that, , according to respondents, the Siza Vieira's Portuguese Pavilion gains aesthetic and comfort characteristics because it uses cork on its facades.

DISCUTION AND CONCLUSIONS

Cork is a material with a wide range of applications and is now becoming increasingly popular due to its sustainable characteristics. It is derived from the bark of a cork oak tree, and understanding the cork oak ecosystem, montado, is essential if we want to use this resource sustainably.

Cork is becoming an increasingly popular material for civil construction due to its many advantages. Not only it is a sustainable material, but it also has excellent insulation, and acoustic and fire-resistant properties. This makes cork a suitable material for using in façades and other parts of the buildings.

Although most of the respondents in this study are aware of the benefits of this type of raw material and its origin, its use in Portugal is in its early stages of development, in what concerns civil engineering. It seems society is ready to introduce this material as an important element in the construction of buildings, but the barriers to this process remain unknown.

This study will be expanded geographically by conducting a similar survey in other populated cities in Portugal where it already exists a building with cork façades.

The collected information will serve as a basis for future research. For example, the economic direction seems to be interesting, namely the analysis of the availability of building materials based on cork, their price, the demand for this product, etc. Equally important is the research and innovation of cork-based building materials regarding their quality and versatility.



CSA2023 – Cork in Science and Applications 7-8 September 2023, Espinho, Portugal

[1] Sandak A., Sandak J., Brzezicki M., Kutnar A. Bio-based building skin.2019

[2] Pereira H. Cork: Biology, Production and Users. Elsevier BV (Eds.) Amsterdam 2007

[3] Fortes M.A., Rosa M.E., Pereira H.A. Cortiça. IST Press. Lisboa. 2004

[4] Graça J., Pereira, H. The periderm development in Quercus suber. IAWA Journal, 25:325-335. 2004

[5] Oliveira, V., Rosa, M.E., Pereira, H. Variability of the compression properties of cork. Wood Science and Technology, 48:937-948.

[6] Leite C., Pereira H., Cork-containing barks-a review. Frontiers in Materials 3, 63. 2016

[7] Knapic S., Oliveira V., Machado S., Pereira H. Cork as a building material: a review. European Journal of Wood and Wood Products, 74(6): 775-791. 2016



USE OF EXPANDED CORK IN HELMET FOR MICROMOBILITY

Miguel Mingote^{*(a)}, Fábio A. O. Fernandes^(b), Gabriel Serra^(b) and Eduardo Noronha^(c)

*(a), (b) University of Aveiro
Center for Mechanical Technology and Automation
Campus Santiago, 3810-193 Aveiro, Portugal
e-mail: miguelmingote@ua.pt

^(c) University of Aveiro ID+ - Research Institute for Design, Media and Culture, 3810-193, University of Aveiro, Portugal

Keywords: Expanded Cork, Micromobility, Helmet, Sustainability

Abstract. Micromobility is a current topic that gained traction with the introduction of electricpowered small vehicles, namely electric scooters and bicycles. Analysing current helmets on the market, it became apparent that despite a few prominent products, regular helmets do not go in line with the premises defined by this type of mobility, both due to their form, but most importantly, through their material choice. This article is based on the development of design and engineering research that seeks to find and develop a more sustainable helmet alternative, that could be more attractive to users than the current solutions available and reach the more environmentally focused consumer that does not have a suitable option at the moment. Helmets are typically composed of an expanded polystyrene (EPS) liner, with a polycarbonate (PC) outer shell. This combination of materials makes them effective, and through refined mass production processes, cheap to produce, thus making them easily replaceable. On the other hand, while cheap and effective, these helmets have a significant environmental impact because EPS deforms permanently. Considering the level of energy required by the standard, it can only withstand one impact. Also, the European Standard 1078 requires the helmet to be replaced after an accident, even if damage is not apparent [1]. Additionally, the Consumer Product Safety Commission (CPSC) recommends replacing a helmet every 5-10 years [2]. This is especially concerning from an environmental standpoint because they are challenging to recycle, as different types of materials are used that are hard to separate at the end of life due to the usage

M. Mingote, F.A.O. Fernandes and E. Noronha.

of glues/adhesives and other permanent joining methods that prevent its recyclability. By exploring alternative, more sustainable materials that align with the United Nations 2030 Agenda for sustainable development, Expanded Cork (EC) was found to be a possible alternative to EPS as a lightweight, relatively cheap, and characterized by a negative carbon footprint [3]. EC is typically used for building insulation and sold in the shape of boards, so an attempt was made to explore a solution obtained via CNC milling. The developed helmet proposal comprises a three-part structure, two side parts, and a central band. Machined to form small cubes connected by a thin layer of cork at the base, and then encapsulated by an elastane fabric, sawn to the cork, that fits the head when in use and compacts when stored, for space saving.

- European Standard EN1078. "Helmets for pedal cyclists and for users of skateboards and roller skates". 2012
- [2] CPSC. "Which Helmet for Which Activity?". 2022. https://www.cpsc.gov/safetyeducation/safety-guides/sports-fitness-and-recreation-bicycles/which-helmet-whichactivity
- [3] A. S. Tártaro, T. M. Mata, A. A. Martins and J.C.G. Esteves da Silva. "Carbon footprint of the insulation cork board". Journal of Cleaner Production. vol. 143, pp. 925-932, 2016.



GEOPOLYMER COMPOSITES: A COMPARATIVE STUDY BETWEEN THE USE OF CORK AND SYNTHETIC AGGREGATES

Zélia Alves*, João Carvalheiras*, Luciano Senff†, Ana M. Lacasta*, Inma R. Cantalapiedra*, João A. Labrincha*and Rui M. Novais*

* University of Aveiro

Department of Materials and Ceramic Engineering / CICECO-Aveiro Institute of Materials Campus Santiago, 3810-193 Aveiro, Portugal e-mail: zeliaralves@ua.pt

[†] Federal University of Santa Catarina (UFSC), Department of Mobility Engineering 89.219-600, Joinville, SC, Brazil

 Barcelona School of Building Construction, Universitat Politècnica de Catalunya, Av. Doctor Marañon 44, 08028 Barcelona, Spain

Keywords: inorganic polymer, aggregate, thermal conductivity, sound absorption coefficient.

Abstract. Lightweight geopolymer composites were produced by varying the content of distinct aggregates, attempting to clarify the potential of cork compared with expanded vermiculite, rubber, expanded polystyrene (EPS), and lightweight expanded clay (Leca). The lowest bulk density was observed for the EPS-containing composites, while Leca composites showed the highest mechanical performance. Cork composites combined low thermal conductivity with very high sound absorption coefficient, particularly above 2000 Hz. Although Leca and EPS exhibited the highest specific strength and low thermal conductivity, respectively, their production processes are not only energy intensive but also require non-renewable resources. In contrast, cork is a natural and renewable resource making it a truly sustainable alternative to produce lightweight geopolymer composites envisioned for the construction sector.

INTRODUCTION

The extensive use of ordinary Portland cement as the primary construction material in the building sector has resulted in a considerable share of CO₂ emissions and energy consumption. As a result of the pressing demand for sustainable building materials, lightweight geopolymer concrete has emerged as an alternative due to performance (e.g., chemical resistance, thermal insulation) and environmental reasons [1]. A widely adopted technique to achieve weight reduction in such materials involves the incorporation of lightweight aggregates, most of them synthetic [2]. The use of natural aggregates [3] is a more attractive option due to their much lower embodied energy compared to other materials currently available on the market (e.g., Expanded PolyStirene - EPS, Leca). Incorporating cork, which is a renewable resource, into a geopolymer matrix has been shown to result in multifunctional composites with low density, low thermal conductivity, high acoustic absorption, and good

moisture buffering capacity [4]. This study aimed to assess and compare the effects of incorporating cork with synthetic lightweight aggregates, such as expanded vermiculite, rubber, EPS and Leca on the properties of the produced composites including their geometric density, compressive strength, thermal conductivity and sound absorption coefficient.

MATERIAL AND METHODS

Materials

Cork granules (0.5-2 mm, 64 kg/m³) were supplied by a Portuguese cork industry, while the used synthetic aggregates were expanded vermiculite (1-2 mm, 130 kg/m³), crushed rubber (1-2 mm, 540 kg/m³), EPS (1-2 mm, 25 kg/m³), and lightweight expanded clay aggregate (Leca®) (1-2 mm, 520 kg/m³). To produce the binder, biomass fly ash (FA), provided by a Portuguese pulp and paper plant, was mixed with metakaolin (MK) (ArgicalTM M1200S, Univar®) and then activated using an alkaline solution composed by sodium silicate (SiO₂/Na₂O = 3.1; H₂O = 62.1 wt.%; Quimialmel; Portugal) and NaOH solution (10 M) (ACS reagent, 97%; Sigma Aldrich).

Geopolymer composite synthesis

The alkaline solution was used to activate the fly ash and metakaolin blend (70:30 wt.%). The paste was then mixed with the lightweight aggregates at different volumetric concentrations, determined by the type of aggregate. The resulting paste was then poured into molds and placed within plastic bags to enable curing under ambient temperature and controlled humidity

First A. Author, Second B. Author and Third C. Coauthor. conditions. After 24 hours, the samples were removed from the molds and left to cure at room temperature until the 28th day.

Materials characterization

The bulk density was determined using the sample's mass to volume ratio, while the compressive strength of the specimens was measured using a Universal Testing Machine (Shimadzu model AG-25 TA) operating at a displacement rate of 0.5 mm//min. The thermal conductivity was measured at room temperature using a heat flow meter apparatus in accordance with ASTM C518-04. Three replicates per composition with cubic dimension (4 x 4 x 4 cm³) were used to perform the characterization assays. Acoustic properties of composites, including sound absorption coefficient determination, were evaluated using cylindrical specimens (d = 50 mm; height ~20 mm) in an impedance tube according with the EN ISO 10534-2 standard protocol.

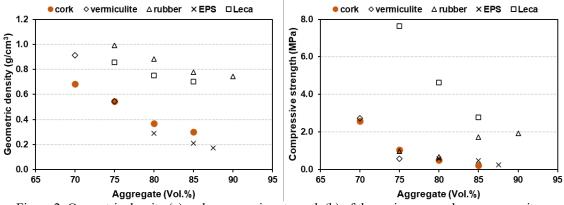
RESULTS AND DISCUSSION

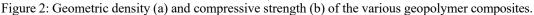
Fig. 1 shows a representative digital photograph of the geopolymer composites containing the

distinct lightweight aggregates. The image illustrates that the aggregates are evenly dispersed throughout the geopolymer matrix, without any segregation or disintegration. Despite the notable geometric density contrast of the aggregates and the binder (1600 kg/m3), the strong surface interaction between them is evidenced. The geometric density of composites decreases as the aggregate content in the geopolymeric matrix increases (Fig. 2), reaching the lowest density (0.17 g/cm3) when EPS is added at 87.5 vol.%. Adding 85 vol.% of aggregate, the composite with cork achieved a density of 0.30 g/cm³, which was 57% lower than Leca and 61% lower than rubber while being 70% higher than EPS. The compressive strength of the composites generally decreased with increasing aggregate content, except for those containing rubber at levels above 80 vol.%, as shown in Fig. 2. This occurs probably due to the elastic behaviour of rubber under compression. At 85 vol.%, adding cork resulted in a compressive strength of 0.2 MPa, which is lower compared to composites containing EPS (0.5 MPa), rubber (1.7 MPa), and Leca (2.8 MPa). Consequently, this leads to a cork containing composite with lower specific strength (compressive strength divided by the sample's density).



Figure 1: Representative geopolymer composites containing cork (75 vol.%), vermiculite (75 vol.%), rubber (75 vol.%), EPS (80 vol.%), and Leca (75 vol.%).





The thermal conductivity of prepared geopolymer composites decreased with the higher aggregate content in the composite. Adding 85% of cork resulted in the lowest thermal conductivity value (68 mW k⁻¹ m⁻¹), being ~ 2.7 times lower than Leca, a commonly used lightweight material in civil engineering, ~ 2.5 times lower than rubber, and roughly 0.3 times than EPS at the same volume fraction. Although EPS-based composites also exhibit excellent thermal conductivity values, EPS is less sustainable than cork due to their fossil origin and emission of toxic fumes when exposed to fire. The sound absorption coefficient of the composites across the frequency range (400-3150 Hz) is provided in Fig. 3. The EPS and the vermiculite composites show poor sound absorption performance, while cork, rubber and Lecacontaining composites show interesting acoustic performance. Leca and rubber composites exhibit the highest sound absorption coefficient between 1000 and 1500 Hz, while the cork composites show higher values than their counterparts above 2000 Hz and up to 3150 Hz.

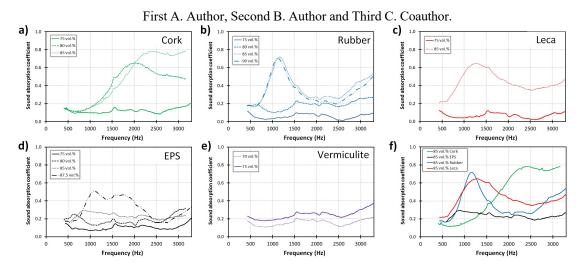


Figure 3: Sound absorption coefficient for the distinct composites. Fig. 3f illustrates the influence of the nature of the aggregate on the sound absorption coefficient for the composites prepared with 85 vol.%.

CONCLUSIONS

This work compared, for the first time, the properties of cork composites with those of synthetic aggregates-containing geopolymer composites. The use of EPS leads to the production of ultralight bodies (0.17 g/cm³), while the use of Leca endows the production of high-resistant samples (7.6 MPa) coupling interesting sound absorption coefficient (1000 – 1500 Hz). On the other hand, cork composites exhibit low density (0.30 g/cm³), the lowest thermal conductivity (68 mW k⁻¹ m⁻¹) and the highest sound absorption coefficient (2000-3150 Hz), which makes them a very attractive option to enhance the thermal and acoustic properties of the building stock while contributing towards the decarbonizing of this building sector.

- [1] Z. Zhang, J.L. Provis, A. Reid and H. Wang, "Geopolymer foam concrete: an emerging material for sustainable construction," *Constr Build Mater, vol.* **56**, pp. 113-127, 2014.
- [2] Z. Alves, J. A. Labrincha, R. M. Novais, "Lightweight Geopolymer Composites: The Impact of the Aggregate," Mater. Proc., vol. 30, no. 13, pp. 1-7, 2023.
- [3] R. M. Novais, L. Senff, J. Carvalheiras, M. P. Seabra, R.C. Pullar, J.A. Labrincha, "Sustainable and Efficient Cork—Inorganic Polymer Composites: An Innovative and Eco-Friendly Approach to Produce Ultra-Lightweight and Low Thermal Conductivity Materials," Cem. Concr. Compos, vol. 97, pp. 107–117, 2019.
- [4] R. M. Novais, J. Carvalheiras, L. Senff, A. M. Lacasta, I. R. Cantalapiedra, J. Giro-Paloma, M. P. Seabra, J. A. Labrincha, "Multifunctional cork alkali-activated fly ash composites: A sustainable material to enhance buildings' energy and acoustic performance," Energy Build, vol 210, pp. 109739, 2020.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). The authors would like to thank the project SMART-G (ERA-MIN/0001/2019), sponsored by FCT.



CORK POWDER RESIDUES VALORISATION BY ADDITIVE MANUFACTURING

Sara P. Magalhães da Silva^{1,2,3*}, Iara Castro^{1,2,3}, António J. Gomes^{1,2,3} and José Martinho Oliveira^{1,2,3}

¹EMaRT Group – Emerging: Materials, Research, Technology, University of Aveiro, Portugal

²School of Design, Management and Production Technologies Northern Aveiro (ESAN), University of Aveiro, Portugal

³Aveiro Institute of Materials (CICECO), University of Aveiro, Portugal

* sarapms@ua.pt

Keywords: Cork Powder; Residues; Additive Manufacturing; Material Extrusion; Binder Jetting

Abstract

Cork is known for its use in wine stoppers. The industrial production of cork stoppers generates cork powder residues with low granulometry ($< 500 \mu m$), which are not feasible for typical cork-based composites. These residues are usually burned. Cork is a natural material, with a Portuguese ID, composed mainly of suberin and lignin. Structurally, it presents an alveolar shape [1]. The combination of its chemical composition and morphology led to a unique combination of properties, which can be highlighted the lightness, compressibility, and thermal and acoustic insulation properties, among others. The upcycling of such cork powder residues is proposed through the development of cork-based formulations adapted for additive manufacturing (AM) technologies. It will combine the cork's unicity with the geometric freedom only attained by AM techniques. More specifically, two AM techniques will be explored and presented, namely Fused Filament Fabrication, an extrusion-based technique and, Binder Jetting (BJ), a powder-based technique. In the case of FFF, cork-polymer composites (CPC) filaments based on polylactic acid [2] and flexible starch-based blends will be presented. For BJ, adapted cork powder-based formulations prepared with hydrophilic additives to tune cork's hydrophobicity will also be discussed [3, 4]. An overview concerning the formulation development, the processing by AM techniques and the post-processing will be presented, together with all the challenges that arose in each phase. In addition, for each AM technique, it will be demonstrated several case studies exploring

intricate geometries not attained by the typical processing technologies of cork-based products.



REFERENCES

[1] H. Pereira, Cork: Biology, Production and Uses. (Elsevier, 2007)

[2] S. P. Magalhães da Silva, T. Antunes, M. E. V. Costa, J. M. Oliveira. "Cork-like filaments for Additive Manufacturing". Additive Manufacturing 34 (2020):101229–101238

[3] S. P. Magalhães da Silva, J. M. Oliveira. "Cork powders wettability by the Washburn capillary rise method". Powder Technology 387 (2021): 16-21.

[4] S. P. Magalhães da Silva, I. Castro, J. M. Oliveira. "Cork Powder Residues processing by Binder Jetting". 3D Printing and Additive Manufacturing (2023):

Iara Castro, Daniel Afonso, António Gomes, Sara Magalhães da Silva and José Martinho Oliveira

Cork filament deposition on freeform surfaces

Iara Castro ^{1,2,3*}, Daniel Afonso^{1,2,4,5}, António J. Gomes^{1,2,6}, Sara Magalhães da Silva^{1,2,3} and José Martinho Oliveira^{1,2,3}

¹EMaRT Group – Emerging: Materials, Research, Technology, University of Aveiro, Portugal ²School of Design, Management and Production Technologies Northern Aveiro (ESAN), University of Aveiro, Portugal ³Aveiro Institute of Materials (CICECO), University of Aveiro, Portugal ⁴ *TEMA* - Centre for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro,

Aveiro, Portugal

⁵ LASI - Intelligent Systems Associate Laboratory, Guimarães, Portugal

⁶ *ID*+ - Research institute of design, media and culture

*iaracastro25@ua.pt

Keywords: Additive manufacturing, 3D printing, freeform surfaces, cork, sustainability

Abstract

Fused Filament Fabrication (FFF) is one of the most widely adopted technologies in the field of additive manufacturing (AM) due to the extensive availability of equipment [1]. Various studies have explored the feasibility of filament deposition on different materials such as fabrics, wood, etc., demonstrating the process's capability of material adhesión [2,3]. Moreover, non-planar approaches have been employed to enhance the adaptability of the process, thereby expanding the design freedom of the products [4]. In parallel, the growing concern for sustainability has led to an increased pursuit of environmentally responsible materials and production processes across various industrial sectors. In this context, cork has emerged as a promising material due to its natural and renewable properties, as well as its sustainable life cycle.

The availability of cork filaments, and the technique of depositing onto cork substrates represents innovative approaches that leverages 3D printing technology to create complex and personalized structures [5]. These techniques allow for the manufacturing of objects using cork as the primary raw material, contributing to a reduction in the consumption of non-renewable resources and a decrease in the associated carbon footprint. Both approaches allow the reuse and valorisation of cork waste, reducing waste and promoting sustainability and circular

Iara Castro, Daniel Afonso, António Gomes, Sara Magalhães da Silva and José Martinho Oliveira economy.

As part of this, a study was conducted to apply advanced knowledge and innovation in FFF printing on freeform surfaces, facilitating material addition and the creation of new forms, as well as the customization of existing parts through substrate digitization, CAD manipulation, and the generation of 3D trajectories for adding new features.

The objective of this work was to explore innovative deposition strategies, such as non-planar deposition on freeform surfaces using FFF, specifically for cork substrates using cork based filaments. This approach enabled material addition, the creation of new forms, and the customization of existing parts. The substrate's surface was digitized, and the CAD design was manipulated to ensure the generation of accurate 3D mixed trajectories for printing over those surfaces. The development process involved the utilization of a Delta Wasp 4020 equipment and the adaptation of the printing head. Multiple deposition strategies were studied and

and the adaptation of the printing head. Multiple deposition strategies were studied and developed, subsequently validated through three case studies involving cork material.

Overall, this research contributes to the advancement of FFF technology, enabling the sustainable manufacturing of cork-based products with enhanced design possibilities and reduced environmental impact.

REFERENCES

[1] Lovo, João, & Fortulan, Carlos (2017). Estudo de propriedades mecanicas e anisotropia em peças fabricadas por manufatura aditiva tipo FDM. SiPGEM – Programa de Pós-Graduação Em Engenharia Mecânica. https://www.researchgate.net/publication/321162555

[2] Me Meyer, Pia, Döpke, Christoph, & Ehrmann, Andrea (2019). Improving adhesion of three-dimensional printed objects on textile fabrics by polymer coating. *Journal of Engineered Fibers and Fabrics*, *14*. https://doi.org/10.1177/1558925019895257

[3] Coe, Edward Olin, Sullivan, Martha, King, Nathan, Kelliher, Aisling, & Williams, Christopher (2019). *Printing on Objects: Curved Layer Fused Filament Fabrication on Scanned Surfaces with a Parallel Deposition Machine*. https://vtechworks.lib.vt.edu/handle/10919/101096

[4] Cendrero, Adrián Martínez, Fortunato, Gabriele Maria, Munoz-Guijosa, Juan Manuel, De Maria, Carmelo, & Lantada, Andrés Díaz (2021). Benefits of non-planar printing strategies towards eco-efficient 3d printing. https://doi.org/10.3390/SU13041599

[5] S. P. Magalhães da Silva, T. Antunes, M. E. V. Costa, and J. M. Oliveira, "Cork-like filaments for Additive Manufacturing," *Addit Manuf*, vol. 34, Aug. 2020, doi: 10.1016/J.ADDMA.2020.101229.

Iara Castro, Daniel Afonso, António Gomes, Sara Magalhães da Silva and José Martinho Oliveira



*

*

CORK STOPPER'S COATING DEPOSITION ANALYSIS USING AN INDUSTRIAL LIBS SYSTEM

M. F. S. Ferreira^{*,†} † * *,† ‡ ‡ ‡ , R. Oliveira , D. Capela , T. Lopes , J. Marrafa , P. Meneses , A. Oliveira ,

C. Batista, T. Gomes, S. Moutinho, J. Coelho, R. Nunes da Silva, D. Guimarães, N. A. Silva

*,†

and P. A. S. Jorge

Center for Applied Photonics, INESC TEC, Rua do Campo Alegre 687, 4169-007, Porto, Portugal e-mail: miguel.s.ferreira@inesctec.pt

[†] Departamento de Física e Astrofísica, Faculdade de Ciências da Universidade do Porto Rua do Campo Alegre 687, 4169-007, Porto, Portugal

[‡] EGITRON, Rua Central da Vergada, 1280, 4535-166 Mozelos VFR, Portugal

• Azevedos Indústria, Rua Santo António 1, 4535-107 Lourosa, Portugal

[•] Cork Technological Centre, Rua Amélia Camossa, 4536-904 Sta. Maria de Lamas, Portugal

Keywords: Laser-induced breakdown spectroscopy, cork stoppers, coating, depth analysis

Abstract

The cork stopper industry serves as an integral part of our daily lives, providing essential sealing solutions for various containers, notably wine bottles. To optimize the sealing performance and facilitate the insertion and removal of cork stoppers, manufacturers typically apply surface treatments, often based on paraffin and silicon compounds. However, existing methodologies for evaluating these surface treatments suffer from drawbacks such as slow analysis, destructive sampling, limited representativity of the batch, and reliance on indirect measurements.

This study introduces a novel approach of employing laser-induced breakdown spectroscopy (LIBS)[1], a micro-destructive technique, for depth analysis of cork stoppers, without compromising the integrity of the samples. The proposed industrial LIBS system prototype enables online analysis of cylindrical-shaped cork stoppers, providing real-time elemental analysis and reducing the time gap between production and batch evaluation.

Herein is present the results obtained with the new CorkSurf LIBS system by demonstrating its effectiveness in evaluating the thickness and uniformity of surface treatment deposition.

ACKNOWLEDGEMENTS

This work is funded by FEDER funds, Portugal, within the scope of the project Corksurf under the reference NORTE-01-0247-FEDER-047040 through the NORTE 2020 Programme.

REFERENCES

D. A. Cremers and L. J. Radziemski, *Handbook of Laser-Induced Breakdown Spectroscopy Second Edition*. John Wiley & Sons Inc., 2013.

EXPANDED CORK IMPREGNATION WITH SHEAR THICKENING FLUIDS FOR LOW-ENERGY IMPACT MITIGATION

Lídia de Oliveira^(a), Rui M. Novais^(b), Ricardo J. Alves de Sousa^(a, b), Fábio A.O. Fernandes^{(a, b)*}

^(a) Center for Mechanical Technology and Automation (TEMA), Department of Mechanical Engineering, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal

^(b) Department of Materials and Ceramic Engineering/CICECO-Aveiro Institute of Materials, University of Aveiro,

Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

^(c) Intelligent Systems Associate Laboratory (LASI), Portugal

*e-mail: fabiofernandes@ua.pt

Keywords: Expanded Cork, Shear thickening fluid, low-energy impact, composite

Abstract. Shear thickening fluids (STFs) are characterized by a nonlinear viscosity increase with the shear rate increase [1]. STFs go from a liquid-like state at lower shear rates to a solid-like state at higher shear rates, characterized by an abrupt rise in their viscosity [2]. Therefore, STF is promising for applications such as shock absorbers, body armour, and vibration insulators. Tan et al. [3] investigated shear-thickening fabric composites (STFC) subjected to stab, drop-weight, Split-Hopkinson pressure bar (SHPB), and ballistic impact. The results showed that STF inevitably flows away from the surface of STFCs without any protection and that shearthickening gel has better stability and is easier to encapsulate. In another study, Kevlar® fabric was impregnated with STF and subjected to ballistic tests. It was possible to conclude there is a significant improvement in ballistic penetration resistance due to the addition of STF. The samples performed equivalently to neat fabric targets of equal areal density while offering significantly less thickness and more material flexibility. Additionally, there is a proportional relationship between the energy absorption by the STF-fabric composite and the STF volume [4]. At this point, it is known that STF synthesis is possible through the mixture of fumed silica nanoparticles and poly(ethylene) glycol, even though there is no specific pattern concerning the synthesis conditions reported in the literature. The STF peak viscosity and critical shear rate depend closely on the concentration of fumed silica, its size, stirring time, and speed [1]. Cork is a natural, fully sustainable, and recyclable material with excellent properties for impact protection applications, which can be tailored for a specific application [5-10]. Cork-STF composite structures have been explored to investigate the potential of impact energy absorption enhancement brought by STF [11-12]. Expanded cork (EC), manufactured with raw material of low quality for stoppers production, is characterised by a negative carbon footprint and lower density than cork polymer compounds. Therefore, this work explores disruptive configurations of EC-based structures strategically enhanced with STF and designed to serve as pads for impact energy absorption purposes. First, several STFs are developed and characterized thanks to rheological tests. Then, EC is impregnated with STF and subjected to low-energy impacts. Results are promising, demonstrating the influence of STF on the impact force and mechanical behavior of the EC-STF composites.

ACKNOWLEDGMENTS

This work was funded by National Funds by FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the project 2022.04022.PTDC. This work is supported by the projects: UIDB/00481/2020 and UIDP/00481/2020 - FCT - Fundação para a Ciência e a Tecnologia; and CENTRO-01- 0145-FEDER-022083 - Centro Portugal Regional Operational Program (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund.

- [1] Bosco, A, Calado, V, Maia, J. Rheological parameters of shear- thickening fluids using an experimental design. Materials Research 2019; 22(5).
- [2] Kang, TJ, Kim, CY, Hong, KH. Rheological behavior of concentrated silica suspension and its application to soft armor. J Appl Polym Sci 2012;124(2):1534–1541.
- [3] Tan, Y, Ma, Y, Li, Y. Shear thickening fabric composites for impact protection: a review. Textile Research Journal 2022;93(5-6).
- [4] Lee, YS, Wetzel, ED, Wagner, NJ. The ballistic impact characteristics of Kevlar woven fabrics impregnated with a colloidal shear thickening fluid. J Mater Sci 2003; 2825–2833.
- [5] Ptak M, Kaczynski P, Fernandes FAO, de Sousa RJA. Assessing impact velocity and temperature effects on crashworthiness properties of cork material. Int J Impact Eng 2017;106: 238-48.
- [6] Fernandes FAO, de Sousa RJA, Ptak M, Migueis G. Helmet design based on the optimization of biocomposite energy-absorbing liners under multi-impact loading. Appl Sci 2019;9(4):735.
- [7] Kaczynski P, Ptak M, Wilhelm J, Fernandes FAO, de Sousa RJAA. High-energy impact testing of agglomerated cork at extremely low and high temperatures. Int J Impact Eng 2018;126:109-16.
- [8] Fernandes FAO, Jardin RT, Pereira AB, Alves de Sousa RJ. Comparing the mechanical performance of synthetic and natural cellular materials. Mater Des 2015;82:335-41.
- [9] Jardin RTT, Fernandes FAOAO, Pereira ABB, Sousa RJA De, Alves de Sousa RJ. Static and dynamic mechanical response of different cork agglomerates. Mater Des 2015;68:121–6.
- [10] Fernandes FAO, Pascoal RJS, Alves de Sousa RJ. Modelling impact response of agglomerated cork. Mater Des 2014;58:499-507.
- [11] Gürgen S, Fernandes FAO, de Sousa RJA, Kuşhan MC. Development of Eco-friendly Shock-absorbing Cork Composites Enhanced by a Non-Newtonian Fluid. Appl Compos Mater 2021;28:165–79.
- [12] Antunes-Sousa GJ, Rocha ARS, Serra GF, Fernandes FAO, Alves de Sousa RJ. Shear Thickening Fluids in Cork Agglomerates: An Exploration of Advantages and Drawbacks. Sustainability 2023; 15(8):6764.