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BOOK OF
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This volume contains the provisional version of the extended abstracts presented at the 13th International Chemical and Biological Engineering Conference (CHEMPOR 2018), held in Aveiro - Portugal, from the 2nd to the 4th of October, 2018.

University of Aveiro & Ordem dos Engenheiros

**13th International Chemical and Biological
Engineering Conference
(CHEMPOR 2018)**

Book of Extended Abstracts

Edited by:

João Araújo Pereira Coutinho

Carlos Manuel Silva

Inês Portugal

Ana Barros-Timmons

Anabela Aguiar Valente

Dmitry Victorovitch Evtyugin

Mara Guadalupe Freire

Pedro Jorge Carvalho



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SCIENTIFIC PROGRAM

Time		Tuesday, 2/10	Wednesday, 3/10	Thursday, 4/10					
8:00	8:15	Registration	Plenary Lecture (PL3) Rajamani Krishna	Plenary Lecture (PL5) Gabriele Centi					
8:15	8:30								
8:30	8:45								
8:45	9:00								
9:00	9:15								
9:15	9:30	Welcome Session	O-BB07	O-EE01	O-IM03	O-RS11	O-EE10	O-BS05	
9:30	9:45								
9:45	10:00	Plenary Lecture (PL1) Nien-Hwa Linda Wang	O-BB08	O-EE02	O-IM04	O-RS12	O-EE11	O-BS06	
10:00	10:15		O-BB09	O-EE03	O-IM05	O-RS13	O-EE12	O-BS07	
10:15	10:30		O-BB10	O-EE04	O-IM06	O-RS14	O-EE13	O-BS08	
10:30	10:45		O-BB11	O-EE05	O-IM07	O-RS15	O-EE14	O-BS09	
10:45	11:00		Coffee-break	O-BB12	O-EE06	O-ME01	Plenary Lecture (PL6) Nikolaos Hadjichristidis		
11:00	11:15	Coffee-break	O-BB13	O-EE07	O-ME02				
11:15	11:30		O-BB14	O-EE08	O-ME03				
11:30	11:45	O-RS01	O-BS01	Bondalti	O-BB15	O-EE09		O-ME04	
11:45	12:00	O-RS02	O-BS02	O-MP01	Lunch	Lunch		Lunch	
12:00	12:15	O-RS03	O-BS03	O-MP02	Keynotes (KN3 and KN4) Adélio Mendes José António Teixeira	Keynotes (KN5 and KN6) Maria Ascensão Reis Ramesh Gardas			
12:15	12:30	O-RS04	O-BS04	Prio					
12:30	12:45	O-RS05	O-BB01	O-IM01	Plenary Lecture (PL4) María José Cocero	Awards and Closing Session			
14:15	14:30	Lunch	Keynotes (KN1 and KN2) João Rocha Rosa Quinta-Ferreira	Keynotes (KN3 and KN4) Adélio Mendes José António Teixeira			Keynotes (KN5 and KN6) Maria Ascensão Reis Ramesh Gardas		
14:30	14:45								
14:45	15:00	O-RS06	O-BB02	BB&G			O-RS16	O-EE15	O-IM11
15:00	15:15	O-RS07	O-BB03	O-MP03			O-RS17	O-EE16	O-IM12
15:15	15:30	O-RS08	O-BB04	BP	O-RS18	O-EE17	O-IM13		
15:30	15:45	O-RS09	O-BB05	O-MP04	O-MP05	O-IM09	O-IM14		
15:45	16:00	O-IM02	O-BB06	O-RS10	O-IM08	O-IM10	O-IM15		
16:00	16:15	Plenary Lecture (PL2) Paul Christakopoulos	Poster Session and Coffee-break P-BB, P-RS, P-MP, P-ME	Poster Session and Coffee-break	Awards and Closing Session				
16:15	16:30								
16:30	16:45	Formal Session with Minister of Economy	Bus to Vista Alegre	Museum Visit	Multibiorefinery Project Meeting (Coffee-break)				
16:45	17:00								
17:00	17:15	Poster Session and Coffee-break P-BS, P-IM, P-EE	Museum Visit	Museum Visit	Multibiorefinery Project Meeting (Coffee-break)				
17:15	17:30								
17:30	17:45								
17:45	18:00								
18:00	18:15								
18:15	18:30	Conference Dinner	Conference Dinner	Conference Dinner	CHEMPOR participants are welcome				
18:30	18:45								
18:45	19:00	Conference Dinner	Conference Dinner	Conference Dinner	CHEMPOR participants are welcome				
19:00	19:15								
19:15	19:30	Conference Dinner	Conference Dinner	Conference Dinner	CHEMPOR participants are welcome				
19:30	19:45								

[PL] - Plenary Lecture
 [KN] - Keynote Presentation
 [RS] - Reaction and Separation Processes
 [BS]- Biorefinery and Sustainability
 [MP] - Modeling, Synthesis and Integration
 of Chemical Processes

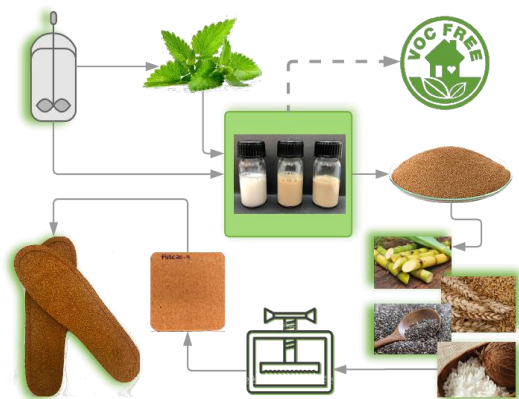
[BB] - Biological Engineering and Biotechnology
 [IM] - Innovative Materials and Applications
 [EE] - Energy and Environment
 [ME] - Multiscale and Multidisciplinary Engineering
 Education

Development of bio- and eco-composites for the footwear industry

P. C. Santos^{1,2,3}, I. P. Fernandes^{1,2}, J. E. Ribeiro², J. M. T. A. Pietrobelli³, M. F. Barreiro^{1,2,*}

¹LSRE-LCM, Polytechnic Institute of Bragança, Campus Santa Apolonia Ap 1134, 5301-857 Bragança, Portugal; ²CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; ³Chemical Engineering Department, Federal University of Technology-Paraná (UTFPR), Campus of Ponta Grossa, 84016-210 Ponta Grossa, PR – Brazil.

*barreiro@ipb.pt



Cork composites are often used in several applications including footwear components. The traditional agglomeration process uses a reactive polyurethane-based binder (containing TDI), generating composites with low flexibility and poor water absorption/desorption characteristics, resulting in products with low comfort properties. Furthermore, the presence of TDI, is another important drawback due to its high toxicity. Therefore, the present work is devoted to the development of cork composites, where the TDI-based binder was replaced by an aqueous PUD reinforced with *Melissa officinalis* L. extract. Cork-composites were produced using different adhesive/cork ratios, and characterized in terms of dimensional stability, water absorption/desorption properties, and mechanical behavior. After the selection of the best adhesive content, composites reinforced with sugarcane bagasse, malt bagasse, coconut fibers, and chia seeds were also produced and characterized.

Introduction

Traditionally, the cork agglomeration process uses a reactive polyurethane-based adhesive, generating composites with low flexibility and poor water absorption/desorption characteristics, resulting in products with low comfort properties. Additionally, this type of binder is based on toluene diisocyanate (TDI), a highly toxic compound. Efforts are being made to replace this adhesive by more environmentally friendly products. In this context, the use of water-based polyurethane-urea dispersions free of NMP (N-methyl-2-pyrrolidone), and exempt of volatile organic compounds (VOC), can be envisaged. Therefore, the present work had as main objective the production of cork composites, where the traditionally used adhesive was replaced by a water-based polyurethane. This former adhesive was synthesized by a process developed at our research group, which generates a final product, both NMP and VOC-free. Moreover, in order to improve composites performance, the adhesive formulation was modified with *Melissa officinalis* L. extracts [1]. Also, water absorption/desorption properties, as well as mechanical properties, were tested as a function of the added biomass residue.

This work is organized according to the following stages: (1) synthesis and characterization of the water-based polyurethane-urea dispersions. Three formulations were produced: base PUD (PUD), and modified PUDs using 3 (PU3C) and 5% (PU5C) (w/w, prepolymer-basis) of *Melissa officinalis* extract. (2) Testing of the adhesive content for composite production. Contents of 20, 30 and 40% (w/w, cork basis; adhesive weight based on its solids content). Following the characterization results, the best adhesive content was selected for further studies; (3) testing of the biomass content: for that composites incorporating 5 and 10% (w/w, cork-basis) of biomass residues (sugarcane bagasse, malt bagasse, coconut fibers and chia seeds), were produced and characterized in terms of stress at break (σ_b) and strain at break (ϵ_b), dimensional stability and water absorption/desorption behavior. The main objective was to select the composites with the best properties, and validate their use in the production of footwear insoles.

Materials and Methods

The *Melissa officinalis* L. dry plant used to produce the extract was purchased in a local market. For the production of the PUD adhesives the following raw-materials were used: Polypropylene glycol with molecular weight 2000 (PPG 2000) as the macrodiol, isophorone diisocyanate (IPDI) as the diisocyanate, 2,2-Bis(hydroxymethyl) propionic acid (DMPA) as the internal emulsifier, triethylamine (TEA) as the neutralizing agent, dry acetone as a co-solvent, 1,2-Ethylene diamine as the chain extender and tin (II) 2-ethylhexanoate (SO) was the catalyst. PPG2000 and DMPA were dried under vacuum at 50°C overnight previously to the synthesis process. The tested biomasses were sugarcane bagasse, malt bagasse, coconut fibers and chia seeds.

***Melissa officinalis* L. extracts obtainment.** The extract of *Melissa officinalis* L. was obtained by the infusion method from dry plant material. Briefly, 20 g of gridded plant was added to 800 mL of boiling distilled water during 5 minutes. The obtained solution was then filtered and freeze-dried, in order to recover the extract in powder form.

PUD synthesis process. PUDs were produced using the modified prepolymer method, developed by Fernandes and co-workers [2]. Three different formulations were produced: base formulation (PUB), and modified formulations with 3 and 5% of *Melissa officinalis* extract (PU3C and PU5C, respectively). The used NCO/OH ratio was 1.7, and DMPA content was 5% (w/w, prepolymer basis). The PUD adhesives (100 g of prepolymer) were synthesized by using a 500mL four neck jacketed reactor equipped with heating, thermocouple and mechanical stirring. The synthesis was carried out under nitrogen atmosphere and the reaction progress was monitored by the dibutylamine back titration method, according to ASTM D 2572-97. Briefly, the required amounts of PPG2000, SO and IPDI were added to the reactor, heated at 80°C under stirring until the theoretical NCO value was reached. Thereafter, the mixture was cooled to 50°C to add the pre-neutralized DMPA in acetone solution. The reaction was left to proceed until the NCO conversion reached the theoretical value. Then the NCO-terminated prepolymer was cooled to 25°C, and distilled water containing the required amount of *Melissa officinalis* added dropwise under vigorous

stirring (prepolymer dispersion phase). The resultant dispersion was heated to 35°C, and EDA aqueous solution (concentration dependent on the NCO conversion after the dispersion stage) added at a flow rate of 0.3mL/min. Finally, acetone was removed in a rotary evaporator (40°C, 350 mbar).

Cork composites production. The composites were produced using a hydraulic press equipped with heated plates and a scale based on 10 g of cork. Two cork granulometries (0.2-0.5mm and 0.5-1mm) were used at a 50:50 ratio. The tested adhesive content (w/w, cork basis; adhesive weight based on its solids content) was 20, 30 and 40% (this content was reflected in the composites nomenclature, e.g. the sample PU3C20 is the composite with PU3C adhesive at a content of 20%). For composites production, first both corks were weighed (5g of each granulometry) and hand mixed. When biomass was added, the applied amount was also mixed with the cork. After, the required amount of adhesive was weighted and added to the previously prepared mixture, and mixed during 10 minutes using a mechanical stirrer. Then, the obtained mixture was transferred to the mold and pressed at 15 bar (135°C), during 2 minutes. After cooling, the mold was open and the composite removed. The samples were stored at ambient temperature during one week, before testing. After the selection of the best adhesive content, cork composites added with residual biomass (contents of 5 and 10%) were produced.

PUD and composites characterization. PUD adhesives were characterized in terms of the produced dispersions and films. For the dispersion, solid content, pH, viscosity, and mean particle size were determined. Films were evaluated concerning chemical structure (FTIR) and thermal behavior (DSC and TGA). Composites were evaluated in what concerns water absorption/desorption behavior and dimensional stability according to the standards ISO 22649:2016 and ISO 22651:2002, respectively. The stress-strain curves and the stress at break (σ_b) and the strain at break (ϵ_b) of the composites were obtained by using a Shimadzu Autograph AGS-X series Europa testing machine.

Results

Table 1 summarizes the properties of the obtained dispersions. The pH values for all the dispersions was around 7, reflecting the absence of free chain extender, showing the good efficiency of the chain extension process. The viscosity values were influenced by the solids content, once a viscosity increment was noticed as the extract content increases. The effect of the extract is also perceptible on the particle size increment, once the PU5C presented higher mean particle size among the three produced PUD formulations (Table 1).

The dimensional stability is evaluated by measuring the length and width of the sample specimen before and after conditioning at 37°C for 24 hours. The established specification for shoe soles requires a variation inferior to 2% (ISO 22651:2002). The obtained results show a change from 0.21% (PU3C20) to 2.33% (PU3C30) for cork composites without biomass, and between 0.21%, for the PUB30 with 5% of malt bagasse, and 2.09% for

the PUB30 containing 10% of sugarcane bagasse, for the biomass containing composites. Biomass addition improves the dimensional stability. For the water absorption/desorption tests, the ISO22649:2016 standard specifies a water absorption higher than 70 mg/cm² and a minimum water desorption of 80%. The water absorption results for the cork composites without biomass varied from 75.12 mg/cm² (PUB20) to 171.38 mg/cm² (PU3C40), while water desorption was between 49.31 (PU3C30) and 80.03% (PU5C20). When biomass is added, absorption values varied from 67.78 mg/cm² (PUB30 with 5% of sugarcane bagasse) to 174.59 mg/cm² (PU3C30 with 10% of coconut fiber), while water desorption varied between 25.72% (PUB30 with 10% of chia seed) to 73.32% (PU5C30 with 10% of sugarcane bagasse). Considering these results, the biomass giving the best effect on water absorption is the coconut fiber at a content of 10%, while for desorption, 10% of chia seeds gave the best results.

Table 1. Results of PUB, PU3C and PU5C characterization.

Sample	pH	μ (mPa.s)	Solids (%, w/w)	Average particle size (μ m)	
				Number	Volume
PUB	7.75	18.55	38.8	0.0157	0.145
PU3C	7.55	61.5	39.7	0.0161	0.107
PU5C	7.55	1878.7	36.59	0.132	2.510

Stress at break (σ_b) and strain at break (ϵ_b) were determined from stress-strain curves of the composites produced with the different adhesive contents. The results are described in Table 2. The highest σ_b values were registered for the composite samples containing 30 and 40% of the adhesives PUD and PU3C, while for the PU5C lower values were obtained. The highest value for σ_b was 0.99 MPa (PU5C30 composite). Based on these results, the selected adhesive content was 30%, once it gave rise to the highest σ_b with both PU3C30 and PU5C30 adhesives.

Table 2. Cork composites mechanical properties.

Sample (*)	σ_b (MPa)	ϵ_b (%)
PUB20	1.10	12.45
PUB30	1.12	15.40
PUB40	1.76	14.56
PU3C20	0.93	14.84
PU3C30	1.13	18.03
PU3C40	1.10	22.11
PU5C20	0.57	13.52
PU5C30	0.99	21.55
PU5C40	0.85	25.45

Conclusions

In a general way, it was observed that water-based polyurethane adhesives presented suitable properties for the production of cork-based composites. The adding of residual biomass increases water absorption/desorption properties.

Acknowledgements

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References

- [1] A. Santamaria-Echart, I. Fernandes, F. Barreiro, A. Retegi, A. Arbelaiz, M.A. Corcuera, A. Eceiza, A., Prog. Org. Coatings 117 (2018) 76–90.
- [2] I.P.M. Fernandes, 2017. Novos Materiais para Calçado Baseados em Poliuretanos e Poliureiras Tese de doutoramento, Universidade do Porto, Porto, Portugal.