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Cork-based composites: studies on binder replacement and incorporation of biomass-derived additives

Hélder M. Rafael[1], Isabel P. Fernandes[1], Bernardo Nunes[2] Vera V. Pinto[3], Maria J. Ferreira[3], Maria Filomena Barreiro[1]

[1]Mountain Research Centre (CIMO) and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnic Institute of Bragança, Campus de Santa Apolonia - 5300-253 Bragança, Portugal
[3]3DCork, Z.I. Pousado, 67, 4535-516 Paços de Brandão, Portugal
[3]CTCP, Portuguese Footwear Technological Center, Rua de Fundões - Devesa Velha, 3700-121 S. João da Madeira, Portugal

Introduction

The Portuguese footwear industry is an important economic sector once it is one of the most active national business areas. The investment made in the production of footwear with high technological performance, and high technical-scientific requirements, evidences the valorization of the footwear industry during the last years. In addition, the evolution of consumers' environmental awareness, allied to the demand for bio-products, is considered a challenge for this sector. Therefore, the development of novel composites, based on natural materials and by adopting green productive processes, represents an area of great interest. In fact, cork, the natural material selected for this application, has properties such as impermeability, good compressibility and resilience, as well as low density, being usually applied in the form of composites for the production of footwear components like shoe insoles and soles. Cork is the bark of a cork oak (*Quercus suber* L.), which is normally harvested every 9-12 years. Among the cork-producing countries, Portugal has the largest annual production, with around 100.000 tons, which represented 49.6% of the worldwide production in 2016 [1]. Traditionally, the cork agglomeration process uses a reactive polyurethane-based adhesive, which results on composites with low flexibility and poor water absorption/desorption characteristics, generating products with low comfort properties. In addition, this adhesive is based on toluene diisocyanate (TDI), which is classified as a high toxic compound, thus motivating its replacement by environmental friendly products. Herein, the use of green adhesives such as water-based polyurethanes dispersions can be envisaged. Furthermore, the low water absorption capacity of the generated composites is related to the hydrophobic character of the cork itself and the used binder, which results in low absorption of the sweat, promoting a sensation of discomfort when footwear incorporating these materials is used. Considering all the above mentioned, the present work is focused on the production of novel cork-based composites, where the traditionally used adhesive was replaced by commercial water-based polyurethane adhesives. In addition, the effect of incorporating residual biomasses on the water absorption/desorption properties will be tested.

Experimental

The cork-composites production was tested by using two commercial adhesives, DIS a water-based polyurethane adhesive and ACR, an acrylic-based water dispersion, both referred as suitable for this application. The DIS adhesive is a polyether-based product supplied by FLEXPUR, Polímeros de Poliuretano S.A., being characterized by containing a solid content of 36% (w/w). The ACR adhesive was supplied by BASF and characterized by containing a solid content of 40% (w/w). For comparison purposes, a commercially available reactive TDI-based polyurethane adhesive (RPU), typically used for the cork-composites production (solids content 99%) was also used. In a first stage, the adhesives were characterized by FTIR operating in ATR mode. The ACR and DIS adhesives were analyzed in film form, while the RPU was analyzed directly. Particle size was evaluated by laser diffraction.

The biomasses residues used where almond shell (AS) and olive stone (OS). AS was kindly supplied by Amendouro - Comércio e Indústria de Frutos Secos Lda. while the OS was offered by Azeites Milénium Lda. Both biomasses were grounded and the granulometry was measured by using calibrated sieves, having the one used 0.43 mm. Contents of 5, 7 and 10% (w/w, cork-basis) were assayed. The cork-composites were produced by using a total cork weight of 10g while the adhesive contents were dependent on the adhesive type. For the RPU, the used content was 20% (w/w, cork-basis), according to supplier indications. For the DIS and ACR, contents of 20 and 30% (w/w, cork basis; adhesive weight based on its solids content) were tested.

The composites were produced by following the procedure described below, which varied according to the tested adhesive. The first stage is common to all the cases and corresponds to cork weighing. Then, the required amount of ACR and DIS adhesives were weighted and added to the cork, being mixed during 10 minutes by using a mechanical stirrer. Afterwards, the DIS/cork mixture was putted in an oven during 15 minutes at 80°C, prior to the composites molding. The ACR adhesive did not required any further stage, being the mixture ACR/cork directly molded. For the RPU adhesive, after its addition to the cork, water at a content of 40% (w/w, adhesive-basis) was also added. This mixture was homogenized for 20 minutes using a mechanical stirrer, thereafter held at room temperature for 20 minutes. The next step corresponded to the composites molding, using a hot plates press and an aluminum mold. The press temperature was set at 135°C and the used pressure was 15 bar, during 2 minutes. The composites were then demolded and stored at ambient temperature during one week, for further characterization. For the biomass incorporation tests, the required amounts of AS or OS were weighed and added right after the cork mixture, being the remaining stages maintained. Figure 1 shows the composites production steps.

Fig. 1. *Experimental system used for the production of cork composites, where (1) mixing the cork with the adhesive, (2) pressing, (3) demolding the composite and (4) cork composite*.

The composites were characterized by evaluating flexibility using a simple test (the samples were folded in a half by hand, and the flexibility classified according to minor or higher ease of folding). The water absorption and desorption were evaluated according to the tests described on ISO 22649:2016 and the ISO 22651:2002 standards, respectively, while the tests specifications for assembly insoles are established on ISO/TR 20882 standard. Briefly, for the water absorption/desorption, samples with dimensions of 5.0X5.0 cm were cut, and the area calculated. Then, samples were weighed and immersed in distilled water for 6 hours. After, the samples were removed from the water, the surface dried with filter paper, and weighed. Then, they were left to dry at room temperature for 16 hours, being then weighed. The water absorption was calculated based on the ratio of the difference between the final and initial weight, per unit of area. The desorption was calculated based on the difference between the weight measured after immersion in water and the weight after drying, dividing by the difference between the final and initial weights of the sample. According to ISO/TR 20882 specifications, the sample is classified as having adequate water absorption and desorption properties if the absorption is higher than 70.0 mg/cm^2 and the desorption is at minimum 80.0%. Regarding the dimensional stability (shrinkage) test, rectangular samples were cut (60 mm ± 20 mm x 60 mm ± 20 mm), and the length and width accurately measured, before and after conditioning at 35±1° C, for 24 hours. The dimensional stability was calculated according to equation (1) and (2). The dimensional variation S is the mean value calculated between S_a and S_b. According to the ISO/TR 20882 specification for assembly insoles, a material is considered as dimensionally stable when it exhibits a shrinkage equal or lower than 2.0%.

$$S_a = \frac{a_0 - a_{24}}{a_0} \qquad \text{Eq. (1)}$$

$$S_b = \frac{b_0 - b_{24}}{b_0} \qquad \text{Eq. (2)}$$

Where a_0 is the AB and CD mean distances at the beginning of the test; a_{24} the AB and CD mean distances after conditioning; b_0 the AC and BD mean distances at the beginning of the test; and b_{24} the AC and BD mean distances after conditioning.

Results and discussion

Regarding the adhesives FTIR characterization, the analysis allowed to confirm the acrylic nature of the ACR adhesive, due to the identification of the carbonyl-associated vibration at 1730 cm^{-1} along with the absence of vibrations corresponding to the presence of OH groups (3400 cm^{-1}). For the RPU and DIS adhesives, a characteristic vibration of the NH group detected at 3300 cm^{-1}, along with the vibration at 1720 cm^{-1} assigned to the C=O group, confirmed the urethane-based nature of the adhesive. Regarding to the base composites, the ones produced with the ACR adhesive presented the lowest flexibility for both tested contents (20 and 30%), once it was not possible to fold the composite piece in half without breaking (this for all the produced samples). Based on this result, this adhesive was discharged for composites production. The DIS-based composites, produced with 20 and 30%, had a similar behavior to the ones produced with the RPU adhesive. The dimensional stability of the produced samples using both adhesives was similar, and equal to 0.3%. However due to the high-water content of DIS, and considering the same experimental conditions, it was not possible to produce homogeneous composites when the content was over 40%. Internal heterogeneity was observed when the composites were cut. Comparing the water absorption results described in table 1, the composite produced with 20% of RPU (RPUC) presented an absorption value of 8.2 mg/cm^2, while when using the same content of DIS (DISC), the absorption was 67.3 mg/cm^2. Based on these results, the DIS content was kept constant (20%) for the subsequent studies. This result evidenced the effect of the hydrophilic character of the adhesive on the water absorption, which increased significantly, however kept below the standard specifications (minimum 70 mg/cm^2). The absorption results evidenced the need for further improvement, which require complementary strategies. Regarding the desorption behavior, both samples present a value higher than the specification of 80%.

The achieved results of absorption/desorption, and dimensional stability, when incorporating residual biomass (5, 7 and 10% of AS and OS), are described in table 1. In a general way, for the samples produced with the RPU adhesive, the incorporation of OS increased the water absorption from 8.2 to 17.6 (OS used at a content of 7%). For the desorption, despite the noticed reduction, in comparison with the RPUC, only the sample containing 5% of AS showed a value lower than the specification of 80%.

Table 1. Composites water absorption/desorption and dimensional stability of the cork base formulations (RPUC and DISC) and formulations with the incorporation of 5, 7 and 10% of almond shell (AS) and olive stone (OS).

Sample (*)	Water absorption (mg/cm^2)	Water desorption (%)	Sa	Sb	S
RPUC	8.2	89.0	0.5	0.0	0.3
DISC	67.3	83.4	0.5	0.0	0.3
RPUAS5	7.8	78.5	0.0	0.0	0.0
RPUAS7	7.9	80.8	0.0	0.0	0.0
RPUAS10	13.1	81.7	0.0	0.0	0.0
RPUOS5	10.6	86.0	0.0	0.0	0.0
RPUOS7	17.6	86.2	0.0	0.0	0.0
RPUOS10	13.9	86.8	0.0	0.0	0.0
DISAS5	63.9	76.0	0.8	1.3	1.0
DISAS7	64.3	75.6	1.3	1.3	1.3
DISAS10	63.7	74.8	0.8	0.0	0.4
DISOS5	58.4	77.9	0.8	0.0	0.4
DISOS7	68.5	88.1	0.4	0.0	0.2
DISOS10	63.5	91.9	0.4	1.3	0.8

(*) RPU or DIS- used adhesive; AS- almond shell and OS – olive stone, the number refers to the biomass content.

For the DIS-based composites, the best result was obtained with the incorporation of 7% of OS, 68.5 mg/cm^2 and 88.1%, respectively for absorption and desorption. The absorption value is close to the specification of 70%, while the desorption fulfils the minimum of 80%. Concerning the dimensional stability, for the RPU-based composites no shrinkage was observed, while for the DIS-base ones, despite being noticed in some extent, results are in good agreement with the specification of 2.0%.

Conclusions

In a general way, it was observed that the water-based polyurethane adhesives (particularly the DIS case) show suitable properties for the production of cork-based composites with improved properties, representing a viable alternative to the TDI-based reactive adhesives. Furthermore, the incorporation residual biomass (particularly OS) lead to a significant increase of the water absorption/desorption capacity, being a simple strategy to improve these properties required for cork-based insoles.

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