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Effects of resin content on mechanical properties of cork-based panels bound with melamine-urea-formaldehyde and polyurethane binders

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ABSTRACT

The properties of agglomerated cork panels bound with melamine-urea-formaldehyde (MUF) and polyurethane (PU) resins were investigated. Tensile strength, Young's modulus, elongation at break, mandrel flexibility, and resistance to boiling water were evaluated. The resins' wettability on the cork surface was also evaluated.

The results showed that resin's nature and content influenced significantly the physical-mechanical properties of the agglomerated cork panels. At the same resin content, panels bound with MUF resin presented considerably higher stiffness and tensile strength when compared to panels bound with PU. On the other hand, PU resin lends resilience and water resistance to the panels, and is the only binder that can be used when panel flexibility is desired.

1. Introduction

Cork is a natural cellular suberous material covering of the species *Quercus suber L.*, commonly known as cork oak and harvested from the tree periodically, usually every 9–12 years, depending on the country [1]. Cork oak forests spread in the western Mediterranean areas of Southern Europe (Iberian Peninsula, south of France and Italy) and North Africa [2]. Cork is a recyclable and renewable source raw material characterized by an interesting combination of properties: low density (120–190 kg/m^3), low thermal conductivity, fire retardant, impermeability to liquids and gases, elastic, resilient and chemically stable material [1–3]. This natural material presents an alveolar cellular structure similar to honeycombs, formed by small regular hexagonal prismatic closed cells as schematized in Fig. 1 [2–5]. The nomenclature used for directions and sections of this material are axial, tangential and radial [2–5]. Chemically, it is mostly composed of suberin (45%), lignin (27%), polysaccharides (12%), ceroids (6%) and tannins (6%) [2–5].

Cork is used in a variety of products as wine bottling stoppers; design and fashion items; construction products as surfacing, flooring and insulation purposes [7]. In many applications, the composition cork is used. This material is made from a mixture of natural cork and an organic resin. The process is carried out under moderate pressure and heating, adequate for the specific polymer curing and bonding [8]. Production of agglomerated stoppers at industrial level can be made through individual molding or continuous extrusion processes [9]. The flooring and surfacing agglomerates are produced from rectangular prismatic blocks or cylindrical blocks. To obtain the final product, the blocks are laminated into boards or subjected to rotary lamination yielding a continuous cork sheet or roll, respectively [10]. The binders include thermosetting resins, such as urea–formaldehyde (UF), melamine-urea-formaldehyde (MUF), phenol-formaldehyde(PF) and polyurethanes (PU) [11]. A specific property just obtained with polyurethane is the higher flexibility of the final panel. However, formaldehyde based resins are three times cheaper and show equality high performance.

The agglomerated cork can be considered a special kind of "wood" based panel and few studies have focused on the behavior of different binders and process variables for its production. Investigations on agglomerated cork composites such as the effect of density on the mechanical behavior of final products [3] and the moisture content and

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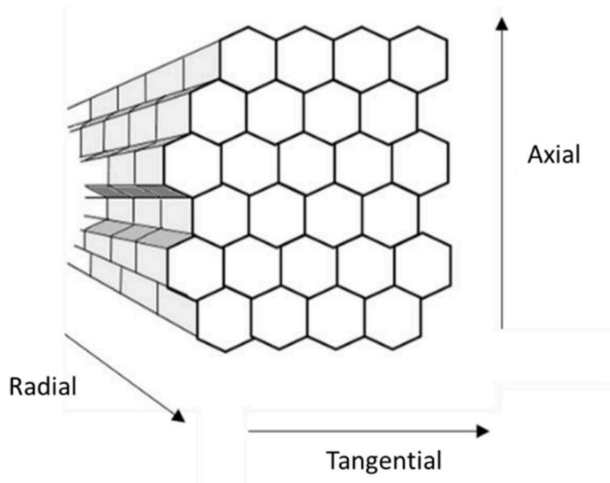

Fig. 1. Schematic representation of cork cells (adapted from Ref. [6].

contact angle of polyurethane in a cork surface have already been studied [9,12–14]. However, several industrial challenges still exist such as: the influence of the nature of the resin on the cork surface and the impact of resin content on the mechanical properties of composites are some of the pertinent questions. Furthermore, there are no reports regarding the use of melamine-urea-formaldehyde resins.

In the case of common wood-based panels, such as particleboard or OSB, there have been several studies relating resin content and other process parameters with the physico-mechanical properties of the final boards [15]. One example are Ayrilmis et al. [16] who studied two types of formaldehyde resins, UF and PF, to investigate the effect of resin type and content (8, 10 and 12 wt %) on the dimensional stability and mechanical properties of particleboards. The authors concluded that increasing resin content, water absorption and thickness swelling decreased for both resins. However, UF particleboard had thickness swelling two times higher than the PF resin bonded particleboard, with the PF resin showing better mechanical properties. Another one is Ozsahin [17], who developed a model for predicting the effects of some production factors such as resin ratio, press pressure and time, and wood density and moisture content on some physical properties of oriented strand board (OSB). The results demonstrated a useful model for predicting some physical properties of the OSB produced under different manufacturing conditions [17]. Also, castor oil based polyurethane resin was tested as an alternative to formaldehyde based resins in particleboards. The aim of the research of Ferro et al. [18] was to evaluate the influence of a castor-oil based polyurethane resin formulation on the modulus of elasticity and modulus of rupture of particleboards. Results showed significant improvements in the modulus of elasticity with increasing pre-polymer component content whilst the modulus of rupture was not affected providing equivalent results for the different proportions of the components of the resin [18]. Similar work using cork was conducted by Santos et al. [19] who determined the influence of production parameters such as binder type (three different diisocyanate based pre-polymers), its quantity, grain size and agglomerate density on the mechanical properties and design requirements of the agglomerated cork.

Agglomerated cork composites are a complex cellular material with high impact in the Portuguese economy. Only a few studies focused on different binders for agglomerated cork panels have been published to date. Neither the application of MUF resins nor their performance comparison with PU resins have been reported. In this work the influence of thermosetting resins of distinct nature were investigated under the same processing conditions. The studied parameters were: resin content at production conditions, contact angle of each resin, flexibility and mechanical properties of panels.

2. Materials and methods

2.1. Materials

Melamine-urea-formaldehyde (MUF) resin and green dye were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal). Physical characteristics of the MUF resin were: 18% of melamine; 64% solid content; pH range of 9.00–10.00 and viscosity range of 200–300 cP (using Brookfield viscosity method – spindle S64).

The conventional resins for low-density cork agglomerates are isocyanate terminated reactive polyurethane prepolymers with a polyether backbone and an average of three functional groups. This type of resin was provided by Amorim Cork Composites, S.A. (Santa Maria da Feira, Portugal). The cork materials were also provided by Amorim Cork Composites, S.A.

2.2. Resin distribution

A mixture of resins and green dye was added to granulated cork at a proportion of 6 wt % of resin content (based on resin solid content). Manual stirring over a 5 min period was done at ambient temperature. Resin distribution was observed by an optical microscopic and photographic camera.

2.3. Contact angle analysis

Contact angles were measured in a DataPhysics Contact Angle System OCA20, a video-based measuring device equipped with software for image analysis, using the sessile drop method. The droplet volume was 4 μl. Contact angles of resins on a pure cork surface were measured during approximately 80 s, at room temperature, allowing the droplets to reach equilibrium. MUF and PU resins were the liquids tested.

2.4. Production and physical-mechanical characterization of agglomerated cork

Agglomerated cork was produced by blending granulated cork with resin (MUF or PU) as described in the section "Resin distribution". The amount of solid resin was 3.8, 5, 6, 12 and 17 wt % based on oven dried cork. After blending, a cork panel was hand formed in a deformable aluminum mold of (2 × 450 x 250) mm. The cork content was determined in order to obtain boards with target densities of 600 kg/m^3. Panels were pressed in a laboratory batch press equipped with both heating and cooling systems, with a set-point in temperature of 150 °C, a pressure of 12 bar, a pressing time of 5 min and a cooling time sufficient to achieve 25 °C. After production, boards were hermetically conditioned until performance evaluation, at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 48 h.

2.5. Physical-mechanical characterization of cork agglomerated panels

2.5.1. Determination of tensile strength, Young's modulus and elongation at break of cork panels

Stress-strain tests were carried out according to International Standard ISO 7322:2000 (E). Three samples with dimensions of (100 × 15 x 2) mm were tested for each production condition at a crosshead speed of 300 mm/min under room temperature. At least three replicates were tested to allow determination of mean values and an assessment of the degree of experimental scatter.

2.5.2. Resistance to boiling water of cork panels

The resistance to boiling water was done according to ISO 7322:2000 (E). Three samples with dimensions of (50 × 50) mm were tested for each resin. The procedure was to place the specimens into boiling water for 3 h. After this treatment, samples were visually examined and classified as disaggregated or not.

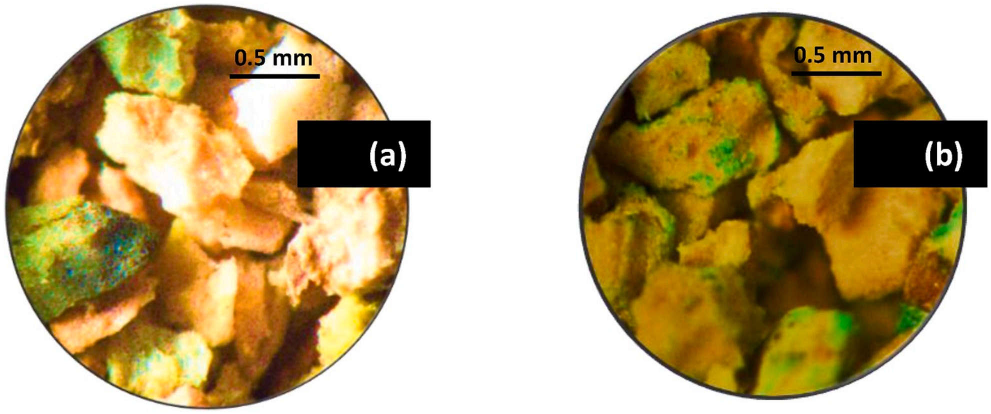

Fig. 2. Optical microscopy photograph of resin distribution in dry cork surface for (a) PU and (b) MUF resins.

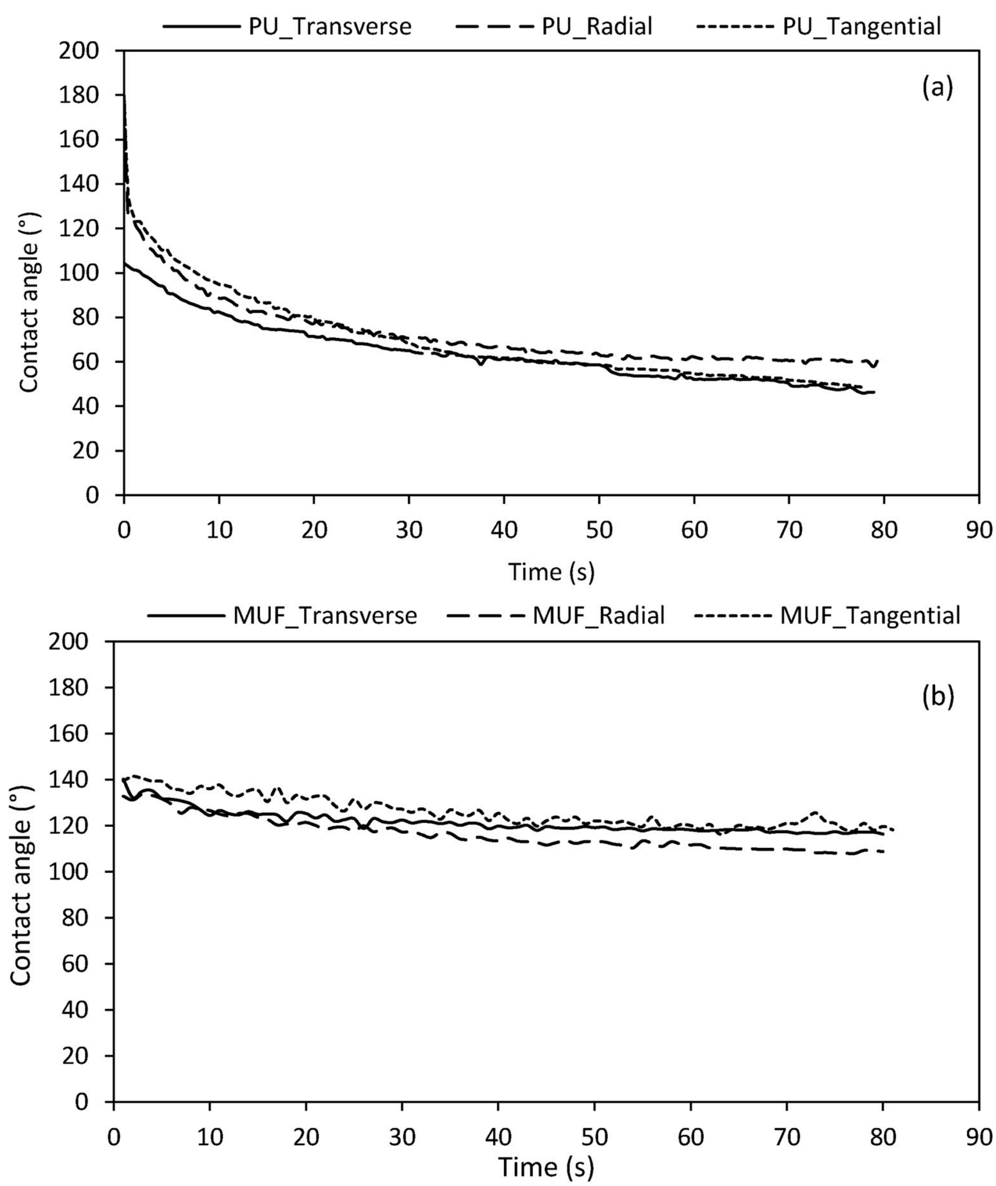

Fig. 3. Contact angles recover over time for three cross sections of cork and two different resins: (a) PU and (b) MUF.

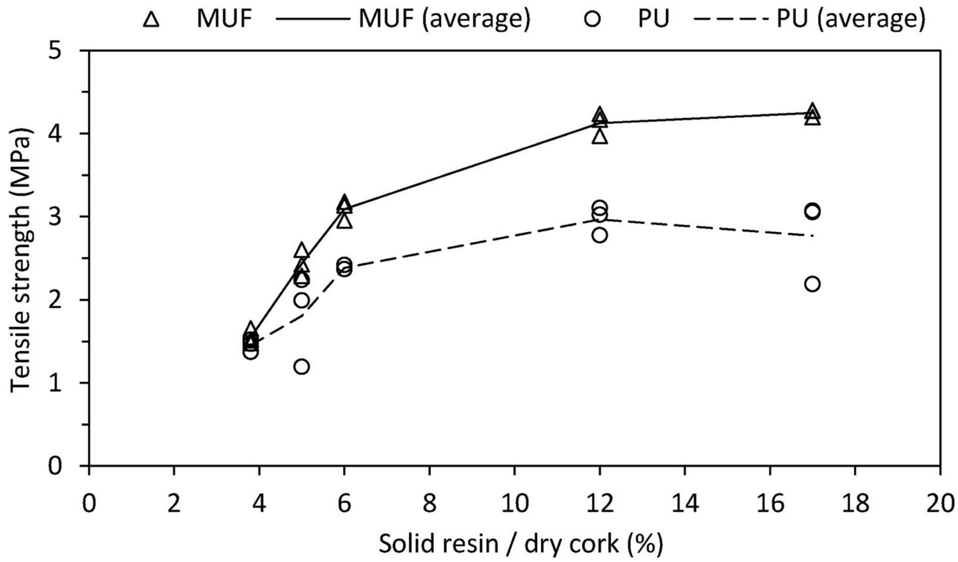

Fig. 4. Tensile strength results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

2.5.3. Flexibility of cork panels

The flexibility of agglomerated cork panels was evaluated following a cylindrical mandrel bending test, according to ASTM F147-87. The method consists in bending the specimen on cylindrical mandrels with different diameters ranging from 3 to 48 mm. The flexibility of the specimen corresponds to the minimum diameter at which the specimen could be flexed without exhibiting any signs of failure.

2.6. Scanning electron microscopy (SEM) of agglomerate cork

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM 35C-Noran Voyager equipment, at CEMUP – Centro de Materiais da Universidade do Porto. The fractured sections of agglomerated cork composite samples, after failure during the mandrel test, were observed. Samples were coated with a gold/palladium alloy before analysis.

3. Results and discussion

3.1. Contact angles and resin distribution

The adhesion of a polymer on cork depends, among other factors, on the wetting of the cork surface by the glue.

After blending granulated cork with MUF or PU, resin distribution on the granulated cork surface was observed by optical microscopy (Fig. 2). The resins were mixed with a green pigment prior to blending with the cork granules. When resin contacts with cork, PU resin disappears immediately but MUF drops roll between cork particles. This difference is evident to the naked eye.

Fig. 2 (a) shows PU performance when mixed with cork particles. Only a few pigmented particles appear in the photo, but these are completely colored, due to the high wettability of PU on the cork surface. MUF resin, on the other hand, does not wet the cork surface easily, which is translated into a nonuniform distribution of resin on the particles' surface – Fig. 2 (b).

To understand this behavior, the contact angles of MUF and PU resins were measured for drops deposited on the radial, tangential and

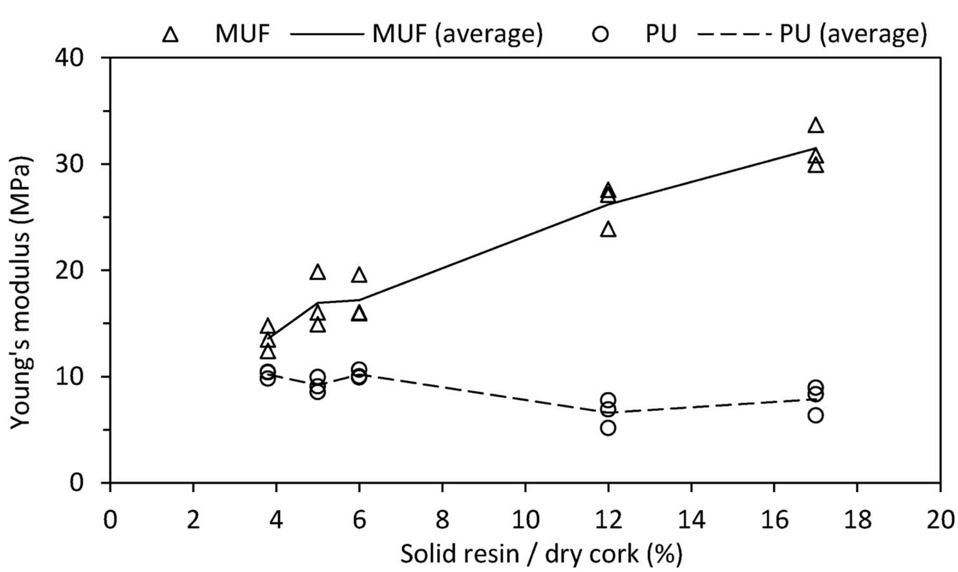

Fig. 5. Young's modulus results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

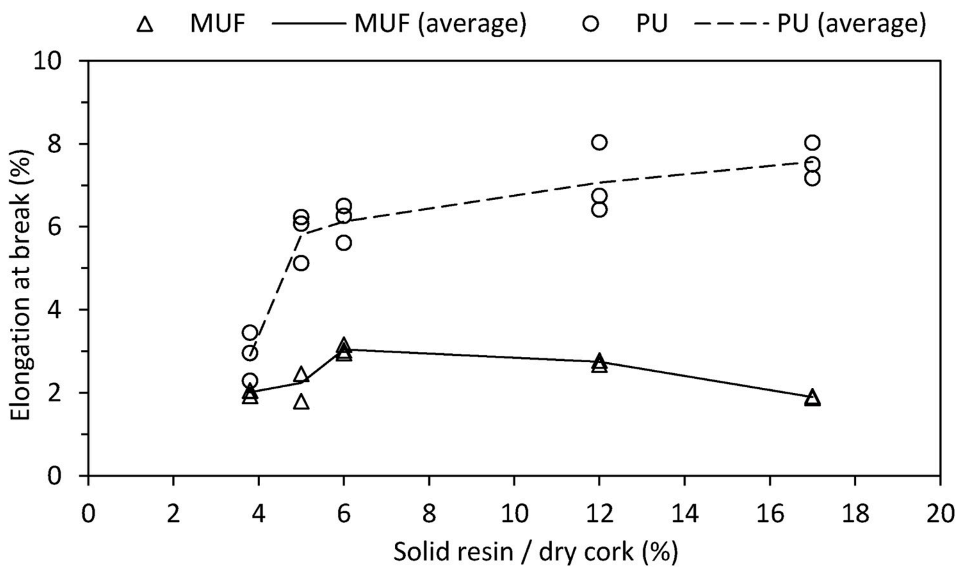

Fig. 6. Elongation at break results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

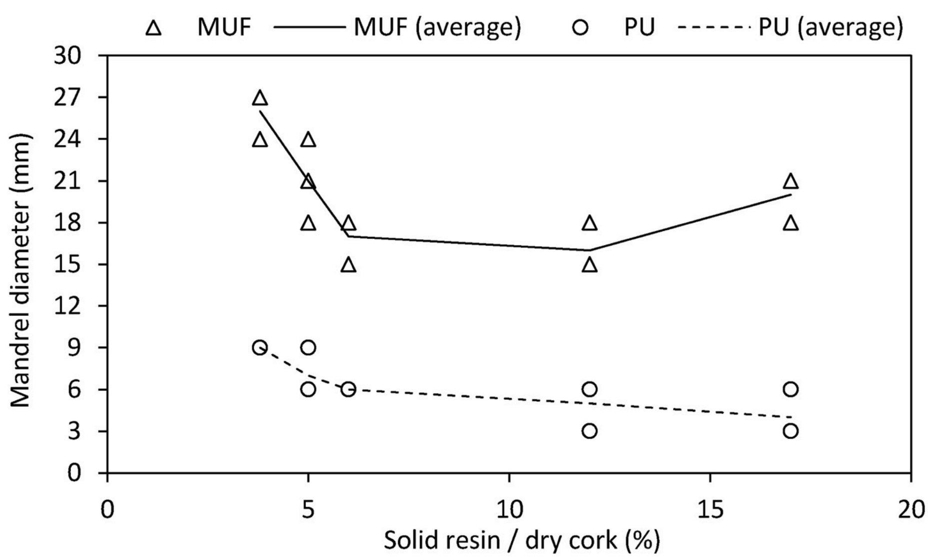

Fig. 7. Mandrel results for MUF and PU cork based panels for different resin contents. The lines join the average values for each content value.

transverse sections of cork samples. Fig. 3 shows the dynamic contact angle results obtained during the first 80 s after drop deposition of MUF or PU resin on cork substrates.

The contact angles, measured on the three sections, were indistinguishable for polyurethane resin. The average contact angles are similar (close to 60°). This indicates that PU resin has good wetting properties on cork surfaces.

MUF resin shows a distinct performance. MUF is a water-based resin and the drops deposited on cork sections show higher contact angles than polyurethane. Cork is hydrophobic due to the presence of suberin and wax compounds. The reported contact angles for water on all sections are close to 100° [20]. For MUF, the contact angles on the three sections were indistinguishable, being close to 120°, showing that cork is not easily wetted by MUF. This is not, however, a negative factor for the resin's performance as a binder in cork composites. When mixed with cork granules, PU drops will immediately wet the surfaces where they land, covering them uniformly. However, since the volume of binder is much lower than the volume of cork, as a consequence the resin will be deposited on only a few granules during the binder/granule mixing process. On the other hand, since MUF does not wet cork as easily, the resin drops tend to roll between the granules during mixing, leaving small fractions deposited throughout several granules. The binder is therefore more uniformly dispersed throughout all granules. A higher amount of PU may therefore be necessary to ensure that all granules receive sufficient resin.

3.2. Physical-mechanical characterization of agglomerated cork

The results of tensile strength, Young's modulus, elongation at break and mandrel flexibility for MUF and PU resins are shown in Fig. 4, Fig. 5, Fig. 6 and Fig. 7, respectively.

As expected, the addition of higher resin content to cork granules increases the tensile strength of all composites. A more noticeable increase is observed between 3.8 and 6 wt% resin content. For higher resin contents, there is a less pronounced increase. MUF resin presents a considerably higher tensile strength compared to PU specimens. One possible explanation for the lower tensile strength with PU is its higher wettability. As discussed above, this may lead to nonuniform

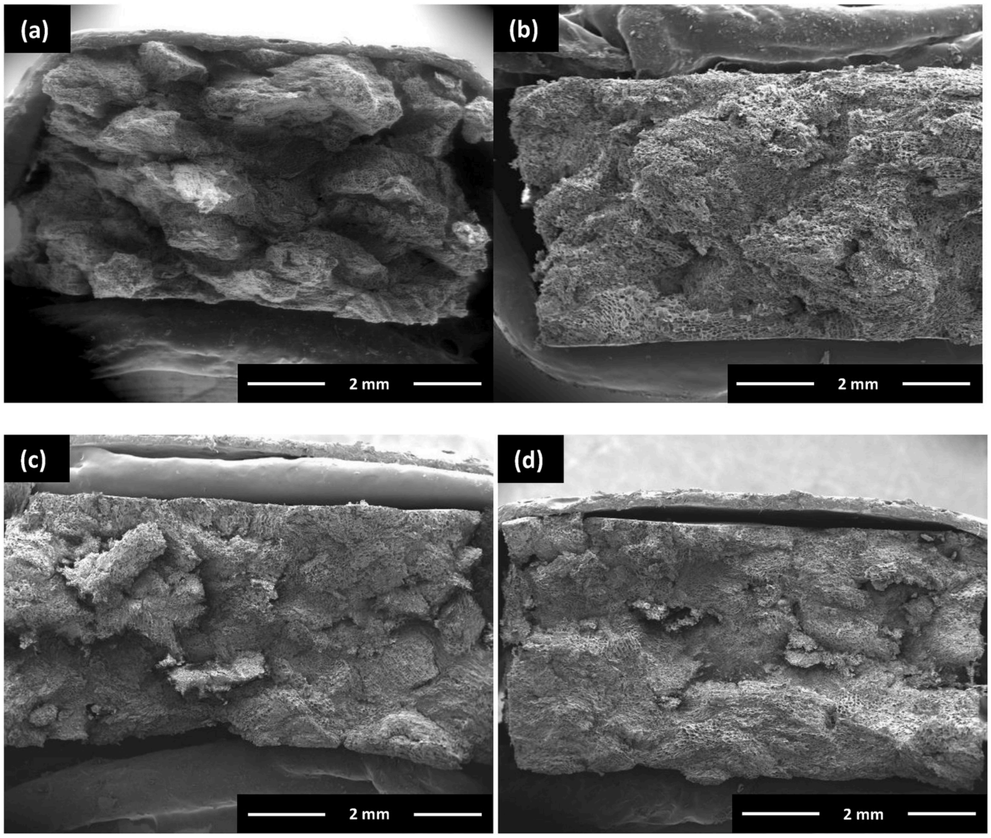

Fig. 8. Micrographs of the fractured surface of cork panels during mandrel test: (a) 3.8 wt % of MUF content; (b) 17 wt % of MUF content; (c) 3.8 wt % of PU content and (d) 17 wt % of PU content.

distribution because the resin is immediately retained on the surfaces that it contacts during the mixing process with no excess resin being distributed on adjacent granules.

As the MUF content increases, the stiffness of the panel increases, resulting in higher Young's modulus. The highly crosslinked structure of the cured MUF resin causes this behavior. On the other hand, with PU the Young's modulus remains essentially constant. PU is a much softer material with low crosslinking, and its elasticity facilitates the relative movement of the cork granules in response to the imposed deformation.

Fig. 6 show the effect of increasing MUF and PU content on elongation at break. When MUF is used, elongation at break increases until 6% of solid resin, because the resin provides better cohesion between the cork granules. When resin content is greater than 6%, the elongation at break decreases. This is a consequence of the stiffness of cork panel with a higher MUF content. With an increase of PU resin content, the elongation at break increases. This is more pronounced with composites prepared with PU contents between 3.8 and 5%. Above 5% PU content, the elongation at break results show a slight increase followed by stabilization, as happens with Young's modulus. This indicates that PU content greatly contributes to the toughness of the composites.

Panel flexibility results (mandrel tests) show the same trend observed in the elongation at break behavior with different solid MUF and PU content (Fig. 7). When using MUF resin with additions between 3.8 and 6 wt% solid resin content, the panel is mechanically weak resulting in breakage at a relatively high mandrel diameter. Between 6 and 12 wt% MUF addition, panel flexibility is better. In this range, panel cohesion is sufficiently high to insure integrity during bending. When resin content is higher than 12 wt%, the rigidity and low resilience of the MUF resin become dominant factors and the panel flexibility is again reduced.

On the other hand, with the increase of PU resin content, the limit mandrel values always decrease. Cohesion improves with resin content and since this is a flexible and resilient binder, there is no detrimental counter effect. It is interesting to note that the tendencies observed in Fig. 7 for the limit mandrel values are qualitatively symmetrical in relation to those of the elongation at break results, both for MUF and PU.

The water resistance of glued cork composites is an important criterion to determine the suitability of the final product for use in humid conditions. Of all specimens, using MUF and PU resins, only the one with lower MUF content (3.8 wt%) did not pass the boiling water resistance test, having been disaggregated.

3.3. Scanning electron microscopy (SEM) of agglomerated cork

Cross sections of cork panels obtained after rupture in mandrel tests were observed. Fig. 8 presents the differences between the cross section of a panel produced with low and high MUF or PU content.

As previously mentioned, 3.8 wt % of MUF content in cork panel is not sufficient to produce a cohesive panel. As a result, upon bending, the individual granules separate and the panel breaks along the granules' interface (glue line). The fractured section results in an irregular surface as shown in Fig. 8 (a). However, when high resin content is used (17 wt %), the glue line between granules becomes much stronger and rupture occurs across the cork granules. This resulting cross section is a homogeneous surface as seen in Fig. 8 (b). Using PU resin, both low and high resin contents lead to homogeneous cross sections – Fig. 8 (c and d).

It can be concluded that the use of a standard MUF resin as a binder in agglomerated cork panels at 6 wt % resin content leads to good mechanical performance. Ultimate tensile strength is actually 55% higher in comparison with PU resin at the same addition level, which has a cost roughly three times higher. However, panel flexibility remains a limiting factor for the MUF resin. The lower mandrel value is 15–18 mm, while with PU a value of 3–6 mm can be attained.

Results corroborate previous studies [19,21–23] which show that the mechanical properties of cork composites are dependent on the type, amount and compatibility between polymeric matrix and cork.

4. Conclusion

The use of melamine-urea-formaldehyde and polyurethane resins for the production of agglomerated cork composites were studied. Polyurethane shows the same wetting behavior independently of the cork section, the average contact angles being close to 60°. MUF resin, being waterborne, presents higher contact angles, close to 120°.

For both binder types, the tensile strength of agglomerated cork panels increases with resin content. MUF resin yields a considerably higher stiffness and tensile strength than PU. On the other hand, panels bound with PU have higher elongation at break, flexibility, and water resistance.

The use of MUF resin as a binder is a more economical alternative than PU, capable of providing good mechanical performance. However, if panel flexibility is paramount, PU may be the only valid option.

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