ROTATIONAL MOLDING OF POLYLACTIC ACID AND AGAVE FIBER BIOCOMPOSITES

D. Rodrigue, Université Laval, Canada

Abstract

In this work, biocomposites of agave fibers (Agave tequilana Weber var. Azul) and polylactic acid (PLA) were produced by rotational molding. In particular, a simple dry-blending technique was used to disperse the agave fibers in the biodegradable polymer matrix. The effect of fiber content was studied (0, 10, 20, 30, and 40 wt.%) and the samples were characterized in terms of morphology, density and porosity to relate with mechanical properties (tensile, flexion, impact and hardness). The results showed that rotomolded biocomposites were successfully produced, but had high porosity leading to lower properties for fiber contents above 10%. It was possible to observe that low fiber contents produced the best morphology, indicating that there is an optimum fiber content to get well-distributed fibers in the matrix.

Introduction

The reduction of crude oil world-wide reserves and the increase of environmental concerns have lead to the use of renewable raw materials such as lignocellulosic materials and biopolymers for the design and development of new and more sustainable components [1]. The development of biodegradable polymers from natural resources provides an excellent opportunity to reduce our dependence on petroleum-based resins such as polyethylene (PE) and polypropylene (PP) [2]. Nowadays, polylactic acid (PLA) is the most used biodegradable polymer because of its bio-based nature, biodegradability and compostability [3]. Despite PLA’s advantages, this polymer presents an important drawback as its mechanical and thermal properties are not stable at higher temperature due to its softening point around 60°C [4]. The reinforcement of PLA with lignocellulosic fibers seems to be a logical alternative in order to increase the mechanical performance and to preserve the environmentally friendly character of the final material [5-7].

Natural fibers have been used to reinforce thermoplastics due to their advantages, such as low cost, low density, acceptable specific strength, good thermal insulation properties, biodegradability, and renewability [8]. However, natural fibers have some disadvantages such as their hydrophilic nature leading to different levels of incompatibility with polymer matrices, as well as low thermal and dimensional stability and high moisture absorption.

Recently, several papers about PLA/natural fibers biocomposites have been published. For example, Dong et al. [9] prepared PLA/coir biocomposites by compression molding and reported tensile and flexural moduli increases (20 and 8%), but tensile and flexural strength decreased (86 and 59%). They also applied an alkali solution to treat the fibers and observed that tensile and flexural strength were improved. Faludi et al. [10] also prepared PLA/wood biocomposites by compression molding and found increases (85%) in tensile modulus with 60% of filler content and decreases in tensile strength (38%). Orue et al. [11] studied the mechanical properties of PLA/sisal biocomposites with different fiber treatments and molded by injection. Their results showed that the tensile strength of PLA could be enhanced by silane treatments by up to 15% for fiber content of 40%, while composites with untreated fiber displayed decreases (43%) compared to neat PLA.

However, despite of all the research reported about PLA/natural fiber composites, there is limited information about this materials obtained by rotational molding. Greco et al. [12-15] evaluated the suitability of processing PLA by rotational molding compared with materials prepared with neat PLA and PLA with a plasticizer [12-13]. Also, they prepared a biocomposite based on plasticized PLA reinforced with a wooden backbone of opuntia ficus indica cladodes [14] and studied the possibility to use PLA with different grades and granulometry for rotational molding processing [15].

An interesting option for rotational molding is to perform a dry-blending step as most materials (polymer matrix and reinforcement) can be obtained in a powder form. Dry-blending is a simple and low cost method to mix different solid components without previous melting steps [16]. In fact, dry-blending is a basic step in most rotational molding industries, as well as for the production of foams and composites [17-19]. It also represents an interesting option for low-thermal stability polymers such as PLA [12,15].
For this reason, this work was dedicated to prepare PLA/agave fiber composites by dry-blending and rotational molding to evaluate the suitability of this process for the production of biocomposites (RBC). Also, the effect of agave content on the biocomposites mechanical properties was studied.

Materials

PLA 3251D from Nature Works LLC was used as the matrix. This biopolymer has a MFI of 80 g/10 min (190 °C/2.16 kg), a density of 1.24 g/cm³, and a melting temperature of 188-210 °C. As reinforcement, agave fibers (Agave tequilana Weber var. Azul) were obtained from a local tequila company (Jalisco, Mexico).

Experimental

Materials preparation

In order to remove impurities and pith, agave fibers were washed in a Sprout-Waldron refiner (D2A509NH) with two discs of 30 cm in diameter, one fixed and the other rotating at 1770 RPM. The fibers were then placed in a centrifuge to remove water, sun dried for 48 hours, grinded and sieved to keep only particles between 297 and 400 µm.

For the dry-blending method, PLA pulverization was necessary. So the pellets were placed in an Arctiko ULTFT 80 ultra-freezer (-80 °C for 48 h) before being milled in a Retsh ZM 200 mill. Powders with an average size between 297 and 400 µm were obtained. It is expected that similar particle sizes of fiber and PLA will limit powder segregation after dry-blending [20].

Dry-blending

Different fiber contents were used between 0 and 40% wt. to study the effect of this parameter on the mechanical properties. To produce the blends, the fibers and PLA were dried at 60 °C for 48 h to remove humidity. Then, a given mass of material (PLA plus fiber) was prepared by dry-blending using an industrial blender (JR Torrey LP-12) for 5 minutes at 3750 rpm. Finally, the blends were oven-dried at 60 °C for 48 h before molding.

Biocomposites preparation

Production of the rotomolded biocomposites (RBC) was carried out in a laboratory-scale rotational molding machine with a cubic stainless steel mold of 15 cm x 15 cm x 16 cm and 2 mm wall thickness. Before loading the material, a demolding agent (CP-500) was applied to the internal surface of the mold. Then, the charged mold was closed, mounted on the rotating arm, and introduced into the oven. The mold was kept rotating for 24 min at 300 °C (heating cycle). Afterwards, the mold was removed from the oven and cooled by forced air for 24 min (cooling cycle). Finally, the mold was opened and the part was demolded. During all the process (heating and cooling) a rotational speed ratio of 4:1 was used with a major axis speed of 3.6 rpm and a plate speed of 2.7 rpm, according to López-Bañuelos et al. [18] and Cisneros-López et al. 2016 [17,21]. The parts were later cut into different geometries to perform all the characterizations using a Guian Gn640MS laser cutter machine.

Density and porosity of biocomposites

Skeletal density was measured by a pycnometer ULTRAPYC 1200e (Quantachrome Instruments) using nitrogen. Bulk density was determined according to ASTM D2395-14, and then porosity was calculated using Equation (1), according to Brewer et al. [22] where \( \rho_s \) represents the skeletal density (determined by the pycnometer) and \( \rho_b \) is the bulk density.

\[
\text{Porosity} (\%) = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100
\]

Morphological characterization

Biocomposite samples of impact fractures test were coated with Au under vacuum during 120 s on a SPI Module Sputter Coater. Then, micrographs were taken on a scanning electron microscope (SEM) TESCAN MIRA3 LMU at different magnifications to characterize the state of fiber adhesion/dispersion in the matrix.

Mechanical properties of biocomposites

Tensile properties were measured on an Instron model 3345 universal testing machine with a 1000 N load cell. Type V samples were cut in the rotomolded parts according to ASTM D638. The crosshead speed was set at 1 mm/min and the reported values for modulus, strength, and elongation at break are based on the average of at least five samples. Flexural tests were performed using a crosshead speed of 1 mm/min and a span to depth ratio of 16 times the average thickness of the samples on an Instron universal tester model 3345 with a 1000 N load cell according to ASTM D790. At least five samples were used to report the average and standard deviation for modulus and strength. The Charpy impact strength was determined by an Instron Ceaast model 9050 impact tester. The specimens were prepared according to ASTM D6110. The values reported represent the average of eight samples notched by a manual sample notcher Instron Ceast 6897 at least 24 h before testing. Hardness was measured with a Titanium 0-90HD durometer according to the Shore D scale (thermoplastics). The reported values are the average of a minimum of ten measurements.

Results and Discussion

Density and porosity of the biocomposites

Figure 1 presents the skeletal and bulk densities, as well as the porosity of RBC samples. The skeletal density increased with fiber content from 1.25 for PLA to 1.30
g/cm$^3$ at 40% of agave fiber content. This increase is mostly related to the higher agave fibers skeletal density of 1.43 g/cm$^3$. Cisneros-López et al. [16] reported similar results for polyethylene reinforced with agave fibers produced by compression molding and rotomolding [16,21]. On the other hand, it was observed that the bulk density of RBC presented important decreases with increasing fiber content: from 1.23 for PLA to 0.48 g/cm$^3$ at 40% fiber. This is associated to the porosity caused by the voids in the biocomposites at high fiber contents since there is no pressure applied on the molten materials while processing [17]. For example, at 40% agave fiber, the biocomposites have a porosity of 61%. The presence of porosity can be explained by the poor adhesion between the fibers and the matrix producing interfacial voids, cavities and defects [23].

Figure 1. Density and porosity of the biocomposites.

**Morphology**

Figure 2 shows the structure of RBC. It was possible to observe that low fiber contents (10-20%) produced the best morphology. This indicates that an optimum fiber content exists to get well-distributed fibers in the matrix. Although higher fiber contents can be used, they generally lead to lower mechanical properties due to fiber agglomeration and porosity, limiting interfacial stress transfer and generating weak zones promoting crack initiation/propagation leading to parts failure [9,25]. To solve this problem, fiber surface treatments or compatibilizers addition should be used [26].

**Tensile properties**

Figure 3 presents the tensile properties of RBC. The tensile modulus of RBC slightly increases from 1908 MPa for neat PLA to 1993 MPa at 10%. However, increasing further the fiber content decreased the moduli by up to 82% (352 MPa) at 40%. These results can be explained by the porosity inside the samples. Rodrigue et al. [27] reported a decrease in tensile moduli of rotomolded samples with increasing wood content, due to the presence of voids and defects inside the composites caused by the incompatibility between the phases and the nature of the processing method (no pressure applied on the compounds in the melt state). The tensile strength decreases with increasing fiber content due to poor adhesion between the agave fibers and the PLA. For 40% RBC, the strength decreased by 90% (from 59 MPa for PLA to 6 MPa), due to their high porosity limiting adequate stress transfer as also reported for PLA biocomposites reinforced with agave, coir and pine [28], sisal [11], bamboo [29], and kenaf [24], as well in polyolefin composites and foams [18-19].

Figure 2. Typical SEM images of the 10% (a), 20% (b), 30% (c) and 40% (d) RBC structure (cross-section).

**Flexural properties**

Figure 5 presents the flexural properties of the RBC. Flexural modulus and strength present similar trends as those reported for tensile properties (Figure 3). Low fiber content (10%) results in a flexural modulus remaining similar to the neat PLA: from 3511 for PLA to 3594 MPa. Again, RBC with higher fiber contents produced inferior flexural properties because of their porosity and defects as discussed above. Similar to tensile strength, flexural strength (Figure 5b) decreased with fiber content: 96% (from 93 MPa for PLA to 4 MPa) at 40% fiber when compared with neat PLA.
Charpy impact strength

Impact strength results are presented in Figure 6(a). A low (10%) fiber content has a positive effect on the composite impact strength (4% higher than PLA), but higher contents decrease the values due to higher porosity as voids are not able to sustain any stresses [19]. The results are in agreement with Cisneros-López et al. [17] reporting increasing impact strength at low fiber content, but important decreases for higher agave contents in rotomolded PE composites.

Hardness

Shore D hardness values are shown in Figure 6(b). The hardness of the biocomposites at low fiber contents (10 and 20%) was similar to neat PLA. However, at higher fiber contents, the hardness substantially decreased. Cisneros-López et al. [17] obtained a similar trend in Shore D hardness for rotomolded composites of agave and polyethylene: i.e. an increase at 10% of fiber followed by an important decrease with increasing fiber content up to 40%. Again, because rotational molding is a low shear/low pressure processing method, the use of higher fiber contents leads to fiber agglomeration and porosity which have a direct effect on the mechanical properties of the composites as discussed in the previous sections.
Conclusions

PLA/agave fibers biocomposites were successfully obtained by dry-blending and rotational molding. It was possible to observe that low fiber contents (10-20% wt.) produced the best morphology, indicating that an optimum fiber content exists to get well-distributed fibers in the matrix. Also, at low fiber contents (10%), the best mechanical properties were obtained. Nevertheless, it would be possible to improve these results by using some coupling agent/fiber surface treatment to improve the fiber dispersion and adhesion in the matrix.

Acknowledgements

One of the authors (E.O. Cisneros-López) acknowledges the financial support of the Mexican National Council for Science and Technology (CONACyT #400517) for a Ph.D. scholarship.

References
