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Properties and processing relationship of polyhydroxybutyrate and cellulose biocomposites

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Abstract

The aim of this work was the development of totally biodegradable composites for using as packaging in food and agriculture industry. Optimum conditions to obtain bilayer composites from polyhydroxybutyrate (PHB) and cellulose cardboard by solvent casting and compression molding were found.

The composites obtained by casting showed lower moisture absorption than the ones made by compression molding, due to the penetration of PHB solution (hydrophobic) into the fibers of cellulose cardboard (hydrophilic).

However, pressed materials showed better mechanical and permeation properties than the composites obtained by casting, because PHB formed a continuous layer on cellulose cardboard.

Mechanical and barrier properties of the composites were optimized, using the least amount of PHB, due to its high cost. The optimum amount of PHB determined was 10 wt% for composites made by casting and 15 wt% for pressed composites.

1. Introduction

Synthetic plastics are resistant to degradation, and consequently their disposal is fuelling an international drive for the development of biodegradable polymers. As the development of these materials continues, industry must find

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novel applications for them. Material usage and final mode of biodegradation are dependent on the composition and processing method employed (Bordes et al., 2009).

Polyhydroxylalkanoates (PHAs) are produced directly from renewable resources by microorganisms. They can be accumulated to high levels in bacteria, and their structures can be manipulated by genetic or physiological strategies. The physical properties and biodegradability of PHAs can be regulated by blending with synthetic or natural polymers. Polyhydroxybutyrate (PHB), the most extensively studied biopolyester, is rather stiff and highly crystalline (Owen and Bergmnann, 2004; Suttiwijitpukdee et al., 2011). The material property of PHB is similar to polypropylene; however, its high melting temperature of 170°C makes the processing of PHB difficult (Cyras et al., 1999; Cyras et al., 2000; Sudesh et al., 2000; Bucci et al., 2005). An important advantage of this polyester is its water vapour barrier property, useful on use as films (Placket and Vázquez, 2004; Shangguan et al., 2006; Sanchez-García et al., 2008; Bordes et al., 2009).

Cellulose is a biodegradable polysaccharide, hydrophilic and not soluble in water or most organic solvents. This polymer is derived from β-D-glucose units, which condense through β(1→4)-glycosidic bonds. The cellulose cardboard is a material widely used in packaging. For specific applications, it is necessary a capability to control the mass exchange of low molecular weight molecules, such as water. Also, cellulose is a potential successful source to use as filler or to form biocomposites (Park et al., 2004; Placket and Vázquez, 2004; Avérousand Le Digabel, 2006; Kalia et al., 2011; Faruk et al., 2012; Khalil et al., 2012). The hydrophilic nature of the cellulose materials is the main drawback of these materials when covering foods (Cyras et al., 2007; Cyras et al., 2009; Talbiet al., 2009).

The aim of this work was to analyze the influence of the processing method (casting and compression molding) on the final morphology, mechanical properties and moisture absorption of biocomposites made of PHB and cellulose cardboard. These biocomposites could replace the commodity polymers used nowadays as packaging, giving relevance to these materials and contributing to the use of polymers from renewable sources derived from vegetal biomass.

2. Experimental

2.1. Materials

Polyhydroxybutyrate (PHB), kindly supplied by PHB Industrial S.A., and cellulose cardboard of jute from Celesa Celulosa of Levante S.A. were used. Chloroform p.a. was purchased from Cicarelli, Argentina.

2.2. Methods

Preparation of bilayer composites by casting

Homogeneous solutions with different amounts of PHB (5, 10 and 15 wt%) in chloroform were prepared by stirring at 60°C. These solutions were poured onto cellulose cardboard in Petri dishes and kept at room temperature for 24 h to eliminate solvent by evaporation. The films were stored at room temperature for 15 days to complete PHB crystallization.

Preparation of bilayer composites by compression molding

The biocomposites of different amounts of PHB (5, 10 and 15 wt%) and cellulose cardboard were obtained by pressing at 50 kg/cm^2 and keeping the temperature at 160°C. Dried films were stored at room temperature for 15 days in order to allow the complete crystallization of PHB.

Bilayer composites characterization

The composites surfaces were coated with a 300 Å gold layer and analyzed by means of scanning electron microscopy (SEM) in a JEOL JSM-6460LV equipment, in order to observed the morphology of the materials.

X-ray diffraction analyses (XRD) were performed with KCu$_\alpha$ (λ=1.54Å) radiation in a Philips PW 1710 X-ray diffractometer. Every scan was recorded at a scan speed of 2º/min with an X-ray tube operated at 45 kV and 30 mA.

Water absorption tests under constant relative humidity environment (RH) were carried out in a hermetic glass box using an aqueous saturated NaCl solution in order to obtain 75 RH% (ASTM E 104-85). Before testing, samples

were dried at 45°C until constant weight (w_0). The weight changes of the samples kept at 75 RH% were measured at different times (w_t). Percent weight change during the test was determined as follows:

$$\%w = \frac{w_t - w_0}{w_0} \cdot 100 \tag{1}$$

where w_0 is the dry initial weight and w_t is the weight at the different times t.

Water vapor permeability (WVP) tests were performed using ASTM E 96-80 method 17. Each film sample was sealed over a circular opening of 0.00177 m^2 in a permeation cell that was stored at 25°C in a desiccator. Anhydrous silica (0 RH%) was placed inside the cell to generate a humidity gradient across the film and the saturated NaCl solution (75 RH%) located in the desiccator. So, the RH inside the cell was always lower than that outside, and water vapor transport was determined from the weight gain by the permeation cell. Weight changes of the cell were plotted as a function of time for all the samples when steady state conditions were reached (about 1 h). Water vapor transmission rate (WVTR) was calculated as the relation between the slope of each curve (g/s), determined by linear regression, and the cell area (m^2). Water vapor permeation (WVP) (g.Pa^{-1}.s^{-1}.m^{-1}) was determined with the following equation:

$$WVP = \frac{WVTR}{S \cdot (R_1 - R_2)} \cdot d \tag{2}$$

where S is vapor pressure of water at saturation (Pa) at test temperature (20°C), R_1 is RH in the desiccator, R_2 is RH in the permeation cell and d is film thickness (m). Each WVP reported was the mean value of at least six samples.

Mechanical properties of composites (dry and conditioned at 75 RH% samples) were determined with an INSTRON 4467 machine. Tensile testing of bone-shaped composite specimens was carried out using a crosshead rate of 2 mm/min (ASTM D 1708-93).

3. Results and discussion

Composites with different amounts of PHB and cellulose cardboard were obtained by compression molding and casting in order to compare their behavior. Fig. 1 shows the micrographs of the composites lateral side obtained by SEM. Fig. 1a correspond to a sample of a bilayer composite obtained by casting with 10 wt% of PHB on cellulose cardboard. It was observed that some of the polymer remained in the surface of the material, while the rest of the PHB penetrated into the cellulose fibers of the cardboard. Alone cellulose fibers were observed in the other surface of the material (Cyras et al., 2007). However, all the PHB remained in the cardboard surface of the sample with 10 wt% of PHB made by compression molding, forming a high density layer of polymer (Fig. 1b) (Cyras et al., 2009).
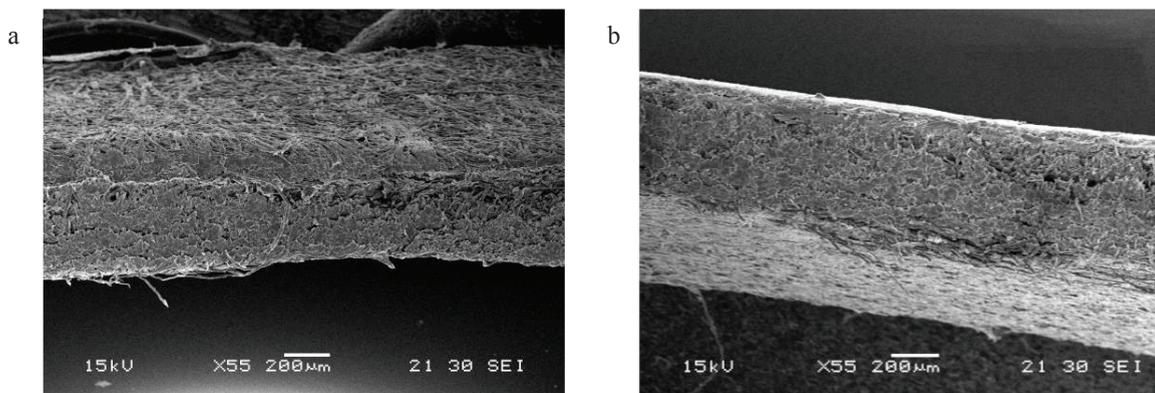

Fig. 1. SEM of lateral surfaces of the composites with 10 wt% of PHB obtained by: (a) casting, (b) compression molding.
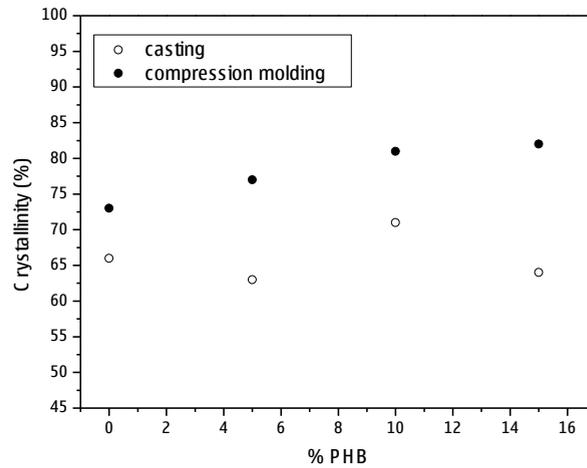
Fig. 2. Percentage of crystallinity of the composites obtained by casting and compression molding.

The percentage of crystallinity of the composites with different PHB amount (Fig. 2) were calculated as the ratio of the peaks area (crystalline phase) and the total area of XRD spectra. These values represent the total crystallinity of the material because the peaks of PHB and cellulose are overlapped. The crystallinity of the pressed composites was higher than that of the ones obtained by casting since the pressing process incremented the crystallinity of the cellulose cardboard.

Fig. 3 shows the percentage of moisture content of PHB films, cellulose cardboard and the composites made by both processing methods. It was observed that PHB film absorbed less water than cellulose cardboard as a consequence of its lower hydrophilicity (Cyras et al., 2007). The composite obtained by casting with 5 wt% of PHB showed a reduction of 15% of moisture content in respect of cellulose cardboard, while pressed films required more than 15 wt% of PHB to reduce a similar moisture content. The composites obtained by casting showed better performance, because PHB penetrates the cardboard fibers, covering it and decreasing the free volume to enter water molecules. Although the hydrophobic layer of PHB on the cellulose cardboard prevents the entry of water in the pressed composites, the presence of some zones with deficient adhesion between PHB and cellulose allowed the more moisture absorption than the casting ones (Cyras et al., 2009).
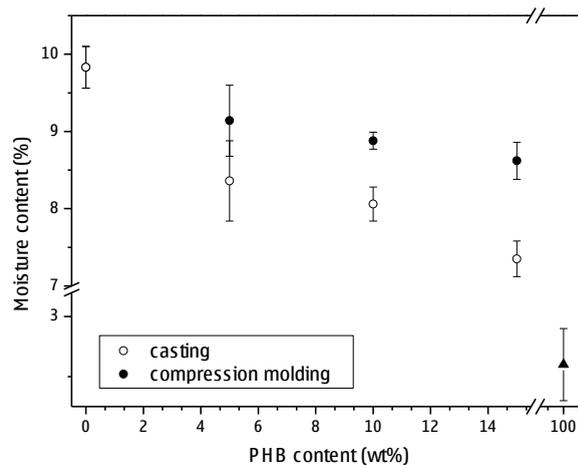

Fig. 3. Percentage of absorbed moisture of the PHB, cellulose cardboard and composites made by casting and compression molding.
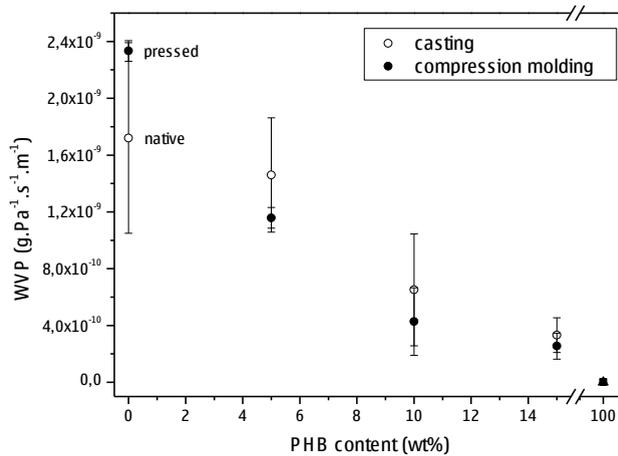
Fig. 4. WVP of the PHB, cellulose cardboard (pressed and native) and composites made by casting and compression molding.

The effect of PHB content on WVP of the composites processed by both methods is shown in Fig. 4. It was observed that the permeation decreased with PHB content due to the hydrophobic character of the polymer (Cyras et al., 2007). Additionally, composites made by casting presented higher permeation than pressed samples. It seems that a continuous layer covering cellulose cardboard is required to reduce water vapor permeation efficiently, as the samples obtained by compression (Fig. 1b). Nevertheless, the samples obtained by casting allowed a higher diffusion of the water molecules through the film bulk than the compressed samples, because the cellulose cardboard surface was not totally covered by PHB (Fig. 1a).

PHB is a brittle material with a Young's modulus of 3,6 GPa, while the cellulose cardboard shows a pull-out behavior with a modulus of 0,88 GPa. The composites showed stress-strain curves similar to those of cellulose cardboard, but they reached higher stress and modulus values, because the interface fiber cellulose-PHB resisted the applied force (Fig. 5). It was observed that the uniaxial tensile behavior of the composites depends on the PHB content. Fig. 6 shows the Young's modulus of the composites with different percentage of PHB obtained by casting and compression molding. The modulus increased with the increment of PHB content. The pressed composites showed higher modulus due to the pressing of the cellulose fibers after compression molding process (Cyras et al., 2007; Cyras et al., 2009).
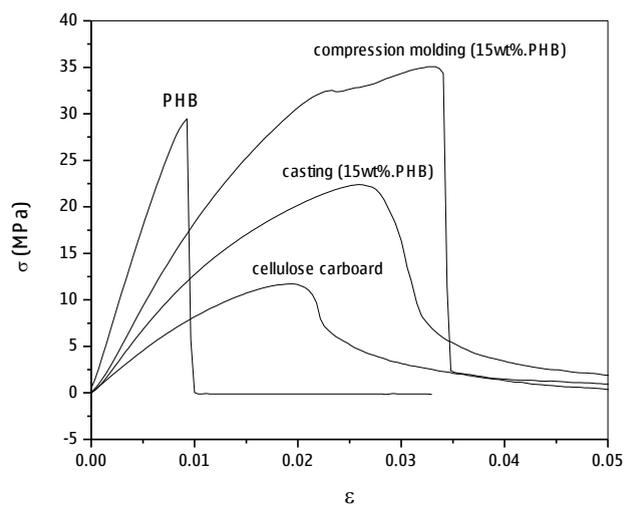

Fig. 5. Tensile curves of PHB, cellulose cardboard and composites with 15 wt%of PHB obtained by casting and compression molding.
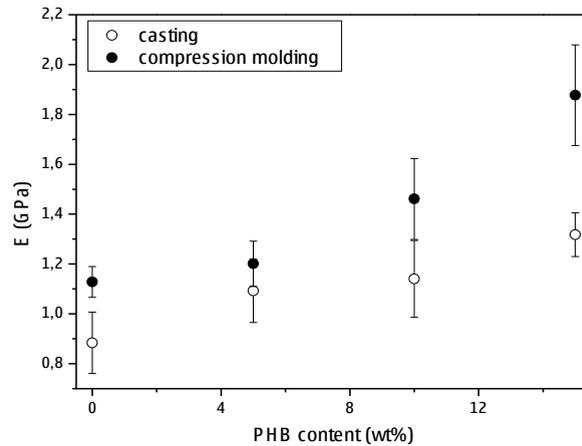
Fig. 6. Comparison of Young's modulus of the composites obtained by casting and compression molding.

To evaluate the influence of the moisture on the mechanical properties of the materials, tensile test was performed on the samples conditioned at 75% relative humidity. This value was compared with the modulus of the dried samples (Fig. 7). In general, the samples obtained by casting presented less diminution in Young´s modulus than molded samples when they were conditioned so, moisture content affected mostly the pressed samples. This could be related to the highest moisture absorption of the pressed composites (Fig. 3), due to the different final morphology obtained by both processing methods.

4. Conclusions

It was possible to develop composites with different morphologies by adding different amounts of PHB to cellulose cardboard by compression molding and casting.

A diminution in the moisture absorption and water vapor permeation of the cellulose cardboard was observed in the composites, because PHB reduces its hydrophilic character. The composites obtained by casting showed better performance in moisture absorption, because PHB penetrates cardboard fibers, decreasing the free volume to penetrate water molecules. However, these samples presented higher water vapor permeability due to cellulose cardboard surface was not completely covered up by PHB. However, hydrophobic PHB covered up the cellulose cardboard in compression molding composites forming a continuous layer in one side of the material, which is able to reduce the sample permeability.
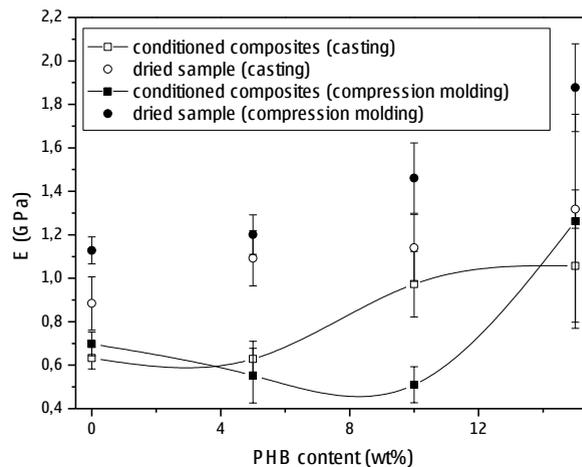

Fig. 7. Comparison of Young's modulus of the dried and conditioned composites obtained by casting and compression molding.

Mechanical properties of biocomposites depended on the PHB content and the processing method, showing a similar behavior than cellulose cardboard, but with high stress and modulus values due to the influence of PHB. Pressed composites presented the highest values. Mechanical properties also depended on moisture content. Samples obtained by casting had improved mechanical properties due to the plasticizing effect of water. Pressed composites absorbed more moisture amount than samples made by casting and moisture effects were greater, influenced by deficient adhesion between PHB and cellulose cardboard.

In this work it was possible to improve the properties of the cellulose cardboard by adding PHB. The pressed composites showed the best performance but it is necessary to achieve a better adhesion between the cellulose cardboard surface and the PHB layer to reduce the moisture absorption. Cellulose cardboard coated with PHB can be developed for the fabrication of food packaging material, with superior barrier and mechanical properties than the cardboard, taking advantage of the good properties of both components.

Acknowledgements

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