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Biocomposites based on renewable resource: Acetylated and non acetylated cellulose cardboard coated with polyhydroxybutyrate

Viviana P. Cyras [a,*], Commisso Ma. Soledad [a], Vázquez Analía [b]

[a] *INTEMA, Instituto de Investigación en Ciencia y Tecnología de Materiales, Facultad de Ingeniería, Universidad Nacional de Mar del Plata, J. B. Justo 4302, Mar del Plata. Argentina*
[b] *INTECIN, Instituto de Tecnologías y Ciencias de la Ingeniería "Hilario Fernández Long", Facultad de Ingeniería, Universidad de Buenos Aires, Las Heras 2214, Buenos Aires., Argentina*

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ABSTRACT

Renewable resource based bilayer films were prepared from polyhydroxybutyrate film (PHB) and cellulose cardboard via compression molding, containing 5, 10, 15 and 20 wt% of PHB.

The effects of PHB contents on moisture absorption, water absorption and water vapor permeation of films were investigated. All biocomposites showed improved permeation properties. As of 15% of PHB, water permeation, equilibrium moisture content and polarity showed a marked drop. It is therefore assumed that the hydrophobic PHB covered up the cellulose cardboard and formed a continuous layer. The water–polymer interactions in materials are critical to the prediction of their behavior in applications where they are exposed to water or humid environment.

The elastic modulus (E), tensile strength (σ) and strain at break (ε) of two-layer biocomposites depend on the PHB content. Improved uniaxial tensile behaviour was obtained in composites with more than 15% of PHB.

In order to improve the adhesion between the cellulose and the PHB, the cellulose cardboard was acetylated. The percentage of moisture absorbed is less than the composites without treatment, due to the better adhesion between the PHB and the cellulose cardboard.

This work showed the studies carried out to obtain and study a new biodegradable bilayer material with the needed amount of PHB to improve the barrier and the mechanical properties of cellulose cardboard. It was demonstrated that two-layer PHB-cellulose films exhibited suitable barrier and mechanical performance for packaging applications, taking advantage of the good properties of both materials. Use PHB coatings should provide an outlet for replace Tetra Pak packaging.

1. Introduction

Concerns in excess of packaging waste have augment interest in biopolymer films and coating. Such films, comprised of polysaccharides, protein, lipid and polyester biodegradable materials, are renewable and can guide to novel packaging request [1–4]. Research findings on production, properties and potential applications of biodegradable films have been reviewed [5,6]. Poly(3-hydroxybutyrate) (PHB) have been attracting much attention in recent years as biocompatible and biodegradable polymer with potential applications [4,5].

The cellulose cardboard is one of the major material distributing in the consumer market. It is used in many applications such as in packaging, structure materials and commodities as well as in hygiene products. But for some application, such as food packaging is necessary a capability to control the mass exchange of low molecular weight compounds between the food and its exterior environment, for example the water [7].

Cellulose is a polysaccharide found in the cell walls of plants fibers and wood, by far the most common polysaccharide is cellulose. Cellulose is hydrophilic, not soluble in water or most organic solvents and biodegradable. Cellulose is a non-branched polymer from β-D-glucose units, which condense through β(1 → 4)-glycosidic bonds. The numerous hydroxyl groups on the glucose residues from one chain form hydrogen bonds with oxygen molecules on another chain, holding the chains firmly together side-by-side and making a structure extremely rigid. This rigidity imparts great strength to the plant and protection to the interiors of plant cells. Several of these polysaccharide chains are given in parallel arrays to form cellulose microfibrils. The individual polysaccharide chains are bound together in the microfibrils by hydrogen bonds and the microfibrils have semicrystal-like properties. The largely organization is of aggregate particles with wide pores capable of holding rather large amounts of water molecules. The hydrophilic nature of the paper–based materials is a main difficulty of these materials when covering moist foods [8].

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[*] Corresponding author.
E-mail addresses: vpcyras@fi.mdp.edu.ar (V.P. Cyras), avazquez@fi.uba.ar (V. Analía).

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Polyhydroxyalkanoates (PHA's), of which poly(hydroxybutyrate) (PHB) is the most common, are carbon energy storage materials produced by many bacteria, in response to conditions of physiological stress. PHA's can be a new start renewable resource based replacement to commodities polymers because of its inherent property as a biodegradable thermoplastic. PHB is well known biodegradable semicrystalline thermoplastic polymer and hydrophobic polyester has many advantages including biodegradability and biocompatibility [9,10]. The PHB is water insoluble and relatively resistant to hydrolytic degradation and is soluble in chloroform and others chlorinated hydrocarbons solvents. However, the practical application of PHB has been restricted by its brittleness and stiffness [11]. A very attractive property of PHB with respect to food packaging applications is its low water vapour permeability, which is close to that low-density polyethylene [8,12,13].

Many study and industrial efforts have been made to use PHB for replaced commodities polymers. However, the PHB films are typically brittle and their production has high cost. Therefore, materials with better mechanical properties and less cost can be prepared by compounding the bioplastic with natural fibers or with other polymers [14].

Poor water vapour barrier ability is generally considered a major limitation to the use of cellulose cardboard as packaging. Barrier properties are one of the most important properties for cardboard packaging containers [15]. The conventional barrier properties for water vapor were developed based on the extrusion products of a range of polymers, such as polyethylene, poly(ethyl terephtalate) or natural wax as well. It is well known that the diffusion processes of different solute and/or solvent membranes depend on the film thickness, structure, crystallinity, preparation conditions, etc. [16,17]. PHB, as a semicrystalline and hydrophobic polymer, may therefore protect cellulose cardboard from moisture sensitivity. In a previous work, we prepared a composite with PHB and cellulose paper by casting. We found that the PHB impregnated the fiber of cellulose, in spite of; to improve the properties is necessary to cover all the paper with PHB [18].

The objective of this work was to fabricate a bilayer biocomposite and to evaluate their barrier and mechanical properties as a function of protective coating of PHB. The biocomposites were fabricated by compression molding. A slender layer of PHB to coat the cellulose cardboard is one possibility to prepare less expensive biodegradable materials with useful properties.

2. Materials and experimental methods

2.1. Materials

Cellulose cardboard of jute from Celesa Celulosa de Levante S.A., was used. Polyhydroxybutyrate (PHB) ($M_n = 42{,}500$) was used, kindly supplied by PHB Industrial S. A., Brazil. Acetic acid glacial (analytical grade) were purchased from Cicarelli, Argentina.

2.2. Experimental methods

2.2.1. Preparation of the bilayer composites

The biocomposites of PHB and cellulose cardboard with different amounts of PHB (5, 10 and 15 y 20%w/w) were obtained by a compression molding, at 160 °C and with a presion of 50 kg/cm^2. The dried films were stored at room temperature for 15 day in order to allow the complete crystallization of the PHB. The biocomposites consist of two layers with PHB at the top and cellulose cardboard at the bottom.

2.2.2. Treatment of cellulose cardboard

The cellulose cardboard was acetylated with acetic acid during 15 min. Then, the samples were washed with ethanol and were dried in an oven at 60 °C to constant weight [19].

Thermal gravimetric analysis was carried out using a Mettler TA 4000 at a heating rate of 10 °C/min under a nitrogen atmosphere with a sample weight of 5–10 mg.

IR-spectroscopy was performed on the composites on the top and bottom sides to study the degree of counting of cellulose cardboard. The apparatus used in this analysis was a Mattson mod Genesis 2, using 32 scans at 2 cm^{-1} resolution, in DRIFT mode. In order to compare spectra of different samples, each spectrum was normalized to the band at 2900 cm^{-1}. This band corresponds to the stretching of CH$_2$ groups; which is insensitive to the composition and degree of crystallinity [20].

X-ray diffraction analysis (XRD) was carried out by means of a Philips 1830/40 diffractometer running with Co K_α radiation ($\lambda = 1.790$ Å) at 40 kV and 30 mA, at 2°/min in the range of 10–55°(2θ).

Contact angle measurements of the surfaces of composites were performed using an MV-50 camera, 6× zoom and acquired with the NIH imaging software Instruments. When a drop of a liquid rests on a solid surface, it forms an angle θ with the surface, called contact angle. Theses angles were performed using a five liquid droplet per samples. In order to establish the surface energy of the PHB and composites, contact angle measurements were performed either with diiodomethane, 99% by Aldrich (purely dispersive nature) and ethylene glycol (99.1% by Aldrich) (polar liquids). The surface energy parameters for the two test liquids are presented in Table 1a.

Under equilibrium conditions, Owens and Went equation [21] has shown that

$$0.5\gamma_2(1+\cos\theta) = \left(\gamma_1^d\gamma_2^d\right)^{1/2} + \left(\gamma_1^p\gamma_2^p\right)^{1/2} \tag{1}$$

where 1 and 2 refers to the solid and liquid respectively; γ^d the dispersive component and γ^p the polar component of the surface energy; θ is the contact angle. If the contact angles made by two liquids of known γ^d and γ^p are measured, it is possible to solve Eq. (1) and infer the γ_1^d and γ_1^p for the material. Then, the total surface energy is estimated from Eq. (2):

$$\gamma_1 = \left(\gamma_1^d + \gamma_1^p\right) \tag{2}$$

Water absorption tests were conducted by immersing the biocomposites films in a water bath at 25 °C (ASTM D570). After immersion in water, the specimens were dried in an oven for 24 h at 50 °C and immediately weighed (to the nearest 0.1 mg). After different time of immersion, the specimens were removed from the water and weighed to the nearest 0.1 mg. The weight of the samples was measured at different times. The moisture absorption was calculated by the weight difference. The percentage weight gain of the samples was measured at different time intervals and the moisture content versus square root of time was plotted. The samples were sealed with silicon on the bottom sides (the sides without PHB), to prevent the entry of water from this side.

2.2.3. Moisture content

Humid environments at 20 °C were prepared in hermetic containers using aqueous saturated NaCl solution to ensure 75% of

Table 1a
Surface energy components of probe liquids for contact angle measurements [17].

(mN/m)	Ethylene glycol	Diiodomethane
Total surface energy (γ)	47.7	50.8
Dispersive component (γ^d)	30.1	48.5
Polar component (γ^p)	17.6	2.3

constant relative humidity environment, according to ASTM E 104-85. The samples were exposed to moisture during different time intervals, and the weight changes were recorded at regular intervals of time. Before the test, the specimens were dried at 45 °C until a constant weight (w_0). The samples were kept at 75% RH and their increasing weight was measured at different times (wt). All the samples were dried until constant weight was determined with a sensitive balance (0.001 g), previously to be exposed to the humid environment [15]. Moisture content was determined as the percentage of initial film weight lost during drying and reported on a wet basis. Triplicate measurements of moisture content were obtained for each type of film and three specimens tested from each film.

The water vapor permeability was determined gravimetrically using an ASTM E 96-95. Film specimens were mounted horizontally on delrin cups filled with anhydrous silica (0% relative humidity (RH). The cups were placed in an environmental chamber at 25 °C and 67% RH. The RH inside the cell was always lower than outside, and water vapor transport was determined from the weight gain of the permeation cell. The cups were weighed every hour for a period of 6 h. Steady state was reached within 1 h. The slopes of the steady state (linear) portion of weight loss versus time curves were used to calculate water vapor transmission rate WVTR, from the slope (g/s) divided by the cell area (m^2). The permeability was calculated from the slope of the steady state straight line of the permeation curves.

Water vapor permeability WVP ($\mathrm{g\,Pa^{-1}\,s^{-1}\,m^{-1}}$) was calculated from:

$$\mathrm{WVP} = [\mathrm{WVTR}/S(R_1 - R_2)] \times d \tag{3}$$

Where S = vapor pressure of water at saturation (Pa) at the test temperature (20 °C), R_1 = RH in the desiccator, R_2 = RH in the permeation cell and d = film thickness (m). Each WVP value represents the mean value of at least five samples for each percentage.

2.2.4. Tensile testing

The mechanical properties of the specimens (dry and conditioned at 75% RH samples) were determined with an Instron Universal Testing Machine (model 4467). Tensile testing of bone-shaped composite specimens was carried out using a crosshead rate of 2 mm/min (ASTM D 882-91). Film tensile strength, percentage elongation at break and modulus was calculated for each type of film, were replicated four times with individually prepared films as the replicated experimental units. Scanning electron microscopy (SEM) images of the fractured surfaces of the samples were obtained by emission scanning electron microscopy (JSM 6100), in order to observe the morphology of the composites.

3. Results and discussions

The Fig. 1 shows the SEM images of the surfaces and fractured surfaces of the PHB and the cellulose cardboard. The PHB showed a compact structure, while the cardboard showed a defibrillated structure with entanglements of fibers.

The results of the thermal gravimetric analysis of the samples are shown in Fig. 2. The degradation of the PHB is characterized by one peak at 261 °C and the cellulose cardboard shows one peak at 357 °C. The peak corresponding to the PHB in the bilayers appears at higher temperature because of the contact between the PHB and cellulose cardboard, which made the PHB more difficult to degrade.

Fig. 3 shows the infrared spectra of samples. To contrast spectra of different samples, the area of the peaks was normalized to 1382 $\mathrm{cm^{-1}}$; which corresponds to the stretching of CH_3 (insensitive to the composition and degree of crystallinity). The cellulose present absorption of the hydroxyl groups at 3460 $\mathrm{cm^{-1}}$. The major PHB bands are the intense ester carbonyl at 1720–1760 $\mathrm{cm^{-1}}$. For the bilayer films, the bottom side spectrum is similar to the spectrum of cellulose cardboard and the top side spectrum is the same that the spectrum of PHB. This indicate that the film of PHB cover all the cellulose cardboard.

The X-ray diffraction pattern of all samples is shown in Fig. 4. The spectra of composites show the peak of cellulose cardboard and PHB. The cellulose cardboard present peak at 15.2, 23.1 and 37° 2θ and the PHB 12.4, 16, 20, 23, 26.3, 32.4 and 49 2θ.

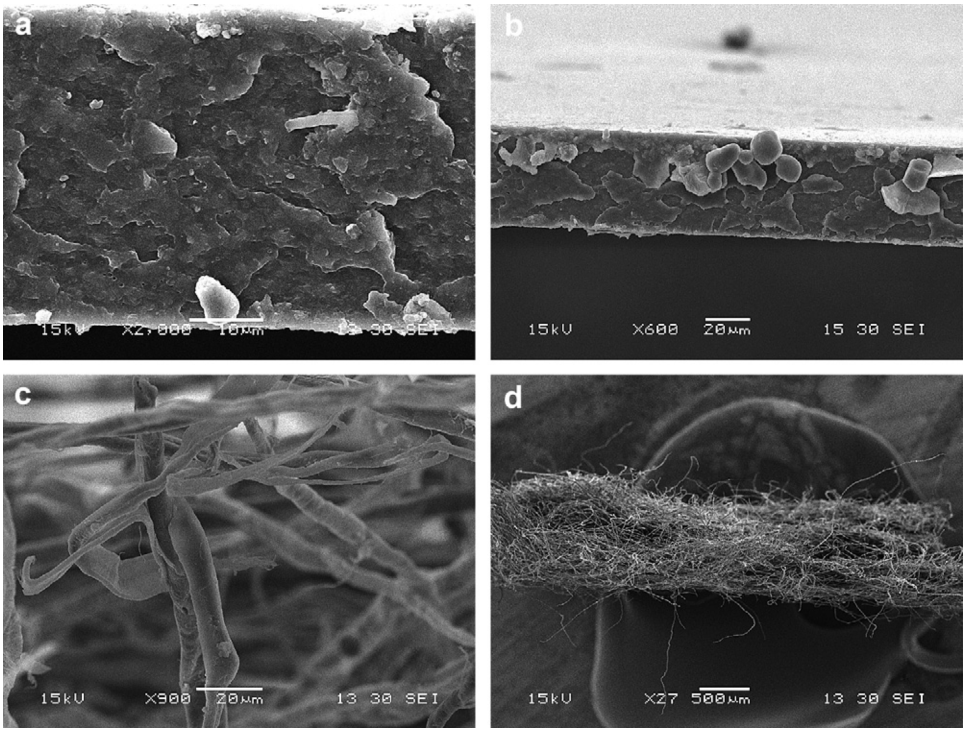

Fig. 1. SEM of surface and fracture surfaces of the PHB and cellulose cardboard.

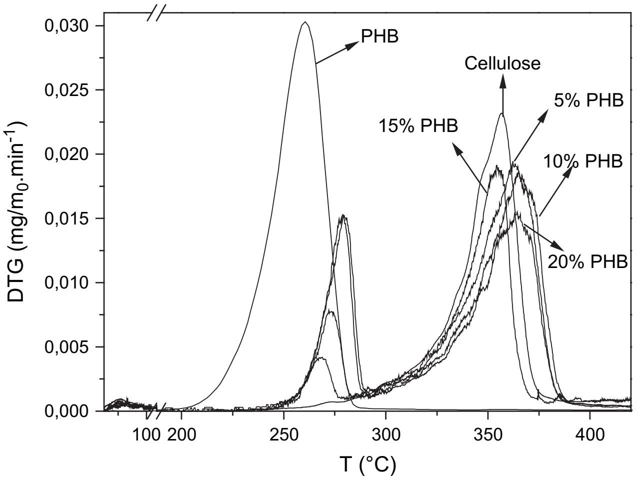

Fig. 2. Dynamic thermal gravimetric analysis at a heating rate of 10 °C/min of: cellulose cardboard, PHB and the bilayer composites.

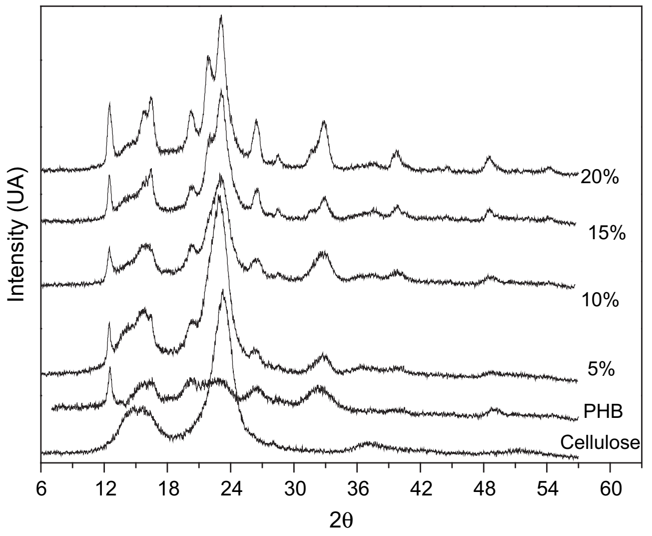

Fig. 4. X-ray diffraction patterns for cellulose cardboard, PHB and their composite films.

The different results between the X-Ray and the infrared analysis is due to the degree of penetration of X-Ray is more extensive of IR. The amount of penetration depends on the energy of the ray and the atomic number, density, and element's mass absorption coefficients. The organic macromolecules have relatively low atomic number and high mass absorption coefficient therefore have high degree of penetration in the PHB.

The surface free energy parameters were calculated using the contact angle of the probe liquids. The polar and dispersive components of the surface energy calculated are shown in Table 1b for the composites and the PHB. A diminution of the polar component was observed and an increment in the dispersive component of the surface energy with the addition of PHB to the cellulose cardboard, because the hydrophobicity of the PHB. In Table 1b it is also shown the polarity of different films, x^p, defined as

$$x^p = (\gamma^p/\gamma) \tag{4}$$

The polarity diminish with the content of PHB since 15%, as of are similar to the value of PHB. It was impossible to measure the contact angle for the cellulose cardboard because the drop was absorbed for the sample, but this effect did not occur in the composites, because the PHB covers the cardboard.

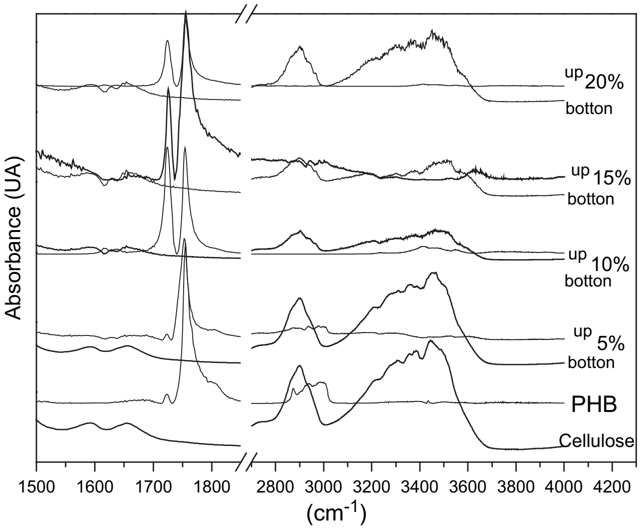

Fig. 3. FTIR spectra of cellulose cardboard, PHB and composites. Normalized to 2933 cm^{-1} peak height.

The micrographs obtained by SEM (Fig. 5) showed, in all composites analyzed, one zone with higher density which corresponds to PHB and another zone which correspond to cellulose cardboard.

3.1. Equilibrium moisture content

In general moisture diffusion in a composite depends on factors such as volume fraction of fiber, voids, viscosity of matrix, humidity and temperature [22]. The moisture content as a function of time was determined in order to measure the equilibrium moisture content of films composites. The percentage increase in weight value (w%) was calculated as follows:

$$w\% = \frac{w_t - w_0}{w_0} \times 100 \tag{5}$$

where, w_t is a wet weight of samples at different times; w_0 is the initial weight of dry samples.

The equilibrium moisture content of the composites films, after conditioning at 25 °C and 50% RH for 5 days, decreased with the addition of PHB (Table 2). This was expected due to the hydrophobic PHB molecules.

3.2. Water absorption value

The percentage of water absorption in the bilayer composites was calculated by weight difference between the samples immersed in water and the dry samples using the following equation:

Table 1b
Surface energy components and polarity of films of PHB and cellulose cardboard +15% of PHB.

Sample	γ^d	γ^p	γ	x^p
PHB	37.94	1.05	38.99	0.03
Cellulose cardboard + 5% PHB	34.74	2.70	37.44	0.07
Cellulose cardboard + 10% PHB	32.39	2.68	35.06	0.08
Cellulose cardboard + 15% PHB	37.45	0.88	38.33	0.02
Cellulose cardboard + 20% PHB	40.92	0.99	41.91	0.02

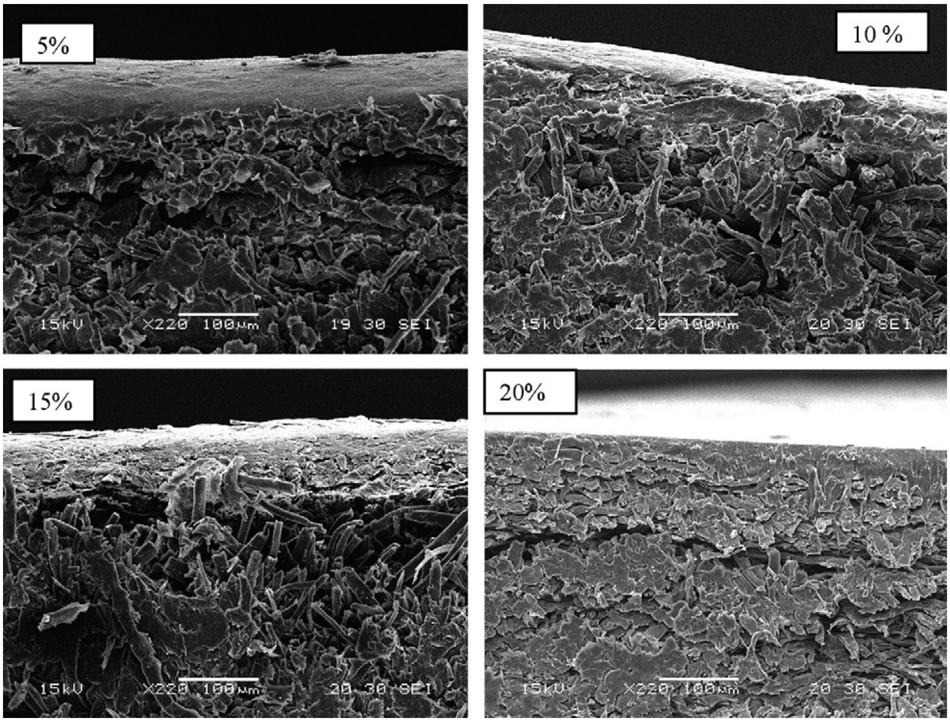

Fig. 5. SEM of fracture surfaces of the composite.

$$w_{\text{in}}\% = \frac{w_{\text{int}} - w_{\text{in0}}}{w_{\text{in0}}} \times 100 \tag{6}$$

where, $w_{\text{in}}\%$ is moisture uptake, w_{in0} and w_{int} are the weight of the specimen before and during immersion, respectively.

Table 2 provides the water absorption of the samples, the percentage of water absorbed decreased with the content of PHB. Again, this is because the PHB is more hydrophobic than the cellulose cardboard. Such good water impermeability also provides resistance of the cellulose to swelling with water, which is one of the most important factors affecting the structural integrity of packaging materials.

3.3. *Water vapor permeation (WVP)*

Table 2 shows the effect of different amounts of PHB on the WVP of cellulose cardboard. Films containing 10% or more PHB had small WVP values. It is necessary that the PHB form a continuous layer on top of the cellulose cardboard in order to be efficient. Similar to moisture content values, this was likely due to the hydrophobic character of PHB molecules, which decreased the rate of sorption and diffusion of water molecules through the film structures.

Table 2
Results of equilibrium moisture content (w_∞), equilibrium water content ($W_{\text{in}\,\infty}$), permeation and polarity for cellulose cardboard and composite films.

Sample	w_∞ (%)	$W_{\text{in}\,\infty}$ (%)	Permeation (g/s m Pa)	Polarity x^{p}
Cellulose cardboard	9.8 ± 0.3	430 ± 50	$2.1 \times 10^{-9} \pm 7.2 \times 10^{-11}$	–
Cellulose cardboard + 5% PHB	9.1 ± 0.5	308 ± 29	$1.1 \times 10^{-9} \pm 7.3 \times 10^{-11}$	0.07
Cellulose cardboard + 10% PHB	8.9 ± 0.1	295 ± 20	$3.9 \times 10^{-10} \pm 6.8 \times 10^{-11}$	0.08
Cellulose cardboard + 15% PHB	8.6 ± 0.2	283 ± 26	$2.2 \times 10^{-10} \pm 7.1 \times 10^{-11}$	0.02
Cellulose cardboard + 20% PHB	8.1 ± 0.6	154 ± 29	$1.9 \times 10^{-10} \pm 8.9 \times 10^{-11}$	0.02
PHB	2.6 ± 0.3	–	$2.3 \times 10^{-12} \pm 7.2 \times 10^{-11}$	0.02

3.4. *Mechanical properties of PHB, cellulose cardboard and bilayer films*

Fig. 6 shows the curves of stress–strain behavior of PHB, cellulose cardboard and bilayer films, containing different amount of PHB. The type of stress–strain curves obtained for the bilayer films are similar to the curves of cellulose cardboard and is typical of pulling the cellulose fiber, but at higher stress values (if the percentage of PHB is bigger than 15%), because the interface cellulose cardboard-PHB resists the applied forces. The PHB is a fragile polymer with a modulus of 3.57 GPa, and the cellulose

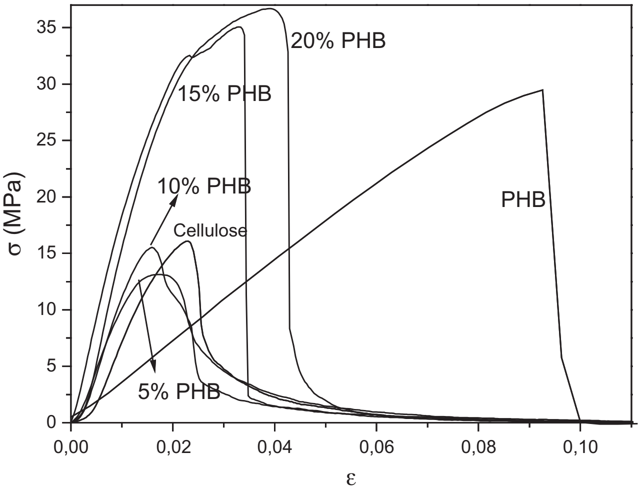

Fig. 6. Tensile test results for the cellulose cardboard, PHB and composite films.

Table 3
Results of the tensile testing of the cellulose's cardboard, PHB and composites with different PHB content.

Sample	E (GPa)	σ_b (MPa)	ε_b (%)
Cellulose cardboard	1.13 ± 0.06	15.4 ± 1.3	21.6 ± 2.5
Cellulose cardboard + 5% PHB	1.20 ± 0.09	13.1 ± 2.5	16.3 ± 2.8
Cellulose cardboard + 10% PHB	1.46 ± 0.16	16.8 ± 1.9	17.8 ± 3.5
Cellulose cardboard + 15% PHB	1.88 ± 0.20	36.8 ± 5.0	34.1 ± 5.6
Cellulose cardboard + 20% PHB	2.04 ± 0.44	38.0 ± 3.3	36.1 ± 4.8
PHB	3.57 ± 0.10	28.9 ± 0.7	10.2 ± 1.2

cardboard shows a delaminating behavior with a modulus of 0.88 GPa. The values of the elastic modulus, stress and strain at break obtained for the bilayer composites are reported in Table 3. The modulus, stress and strain at break increase with the increase of the content of PHB.

Tensile tests were performed on the PHB, the cellulose cardboard and the bilayer films conditioned at 75% HR. The conditioned composites show a lower modulus and tensile stress than the dry samples due to the plasticizer effect of water on cellulose cardboard fibers that produces more relative motion between the fibers in the zone of the cardboard (Fig. 7).

3.5. *Morphology*

SEM micrographs representing the morphology of the cross-sections of the films are depicted in Fig. 5. On the surface of bilayer film were noticeable a compact layer of PHB and then is possible to observe a fiber of cellulose cardboard oriented in random arrangements. The observations by SEM of the fracture surface confirm the pull-out of fibers from the cellulose cardboard.

3.6. *Acetylation of cellulose cardboard*

The interfacial union between cellulose cardboard (material hydrophilic) and the PHB (material hydrophobic) is weak. In order to improve the adhesion between the cellulose and the PHB, the cellulose cardboard was acetylated in the surface.

The acetylated cardboard was characterized by FTIR analysis. This analysis provides information about the efficiency of chemical modification. Spectra in Fig. 8 show the differences between bands before and after fibers acetylation. The main change of treated fibers in comparison to untreated fibers spectra is related to the appearing of band at 1705 cm^{-1}, this band is proceeding from wide C=O carbonyl peak from bonded acetyl group. Moreover, bands at 1030 cm^{-1}, proceeding from C–O alcoholic stretch and at 1380 cm^{-1} from C–H from cellulose and hemicelluloses are observed in both spectra. In chemical modification, the hydrogen of hydroxyl group was substituted by acetyl groups, resulting in lower hydroxyl groups and lower hydrophilicity.

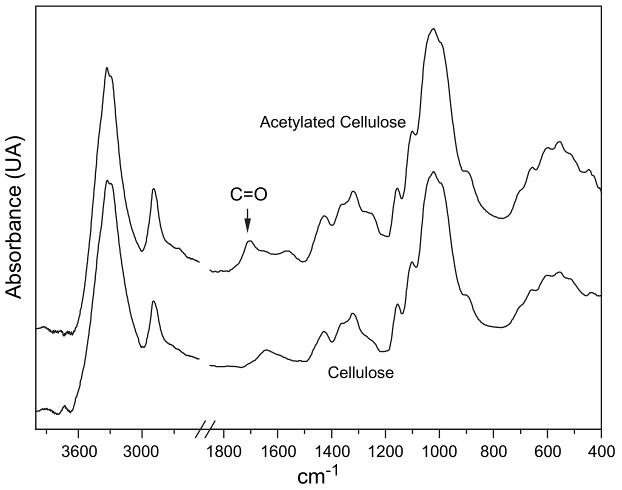

Fig. 8. FTIR spectra of native and acetylated cellulose. Normalized to 2933 cm^{-1} peak height.

The Fig. 9 shows the effect of treatment in the absorption of water. The percentage of water is less than the composites without treatment, due to the better adhesion between the PHB and the cellulose cardboard.

In all the cases the elastic modulus and elongation were small in the untreated samples, due to the treatment influence in the cellulose bulk (Fig. 7) [19]. Therefore, the treated materials do not show an increase in the mechanical properties, in spite of the increment in the adhesion and the decrements in the absorption of moisture. The procedure should be improved in order to treat only the surface without affecting the bulk.

The SEM micrograph of bilayer composite with cellulose treated shows more effective cellulose matrix adhesion (Fig. 10). It can be

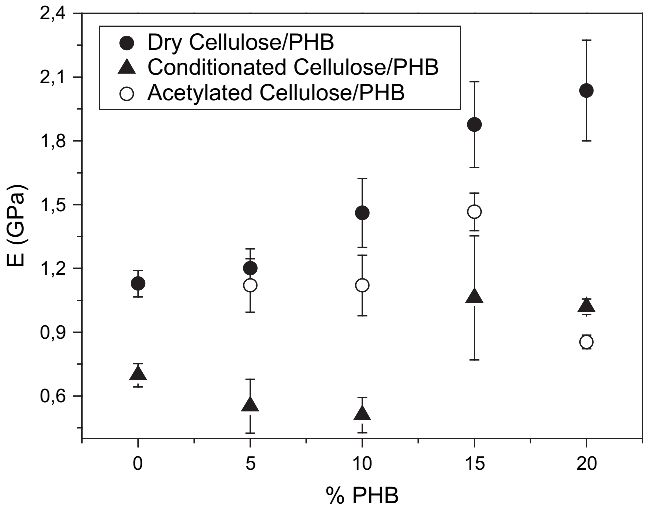

Fig. 7. Modulus of dry cellulose cardboard/PHB, conditioned cellulose cardboard/PHB and acetylated cellulose cardboard/PHB composite films.

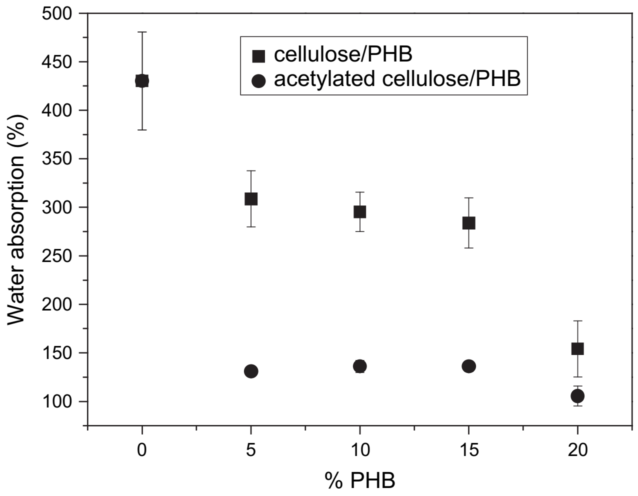

Fig. 9. Percentage increase in weight value (wt%) at 75% HR of: cellulose cardboard/PHB and acetylated cellulose cardboard/PHB composite films.

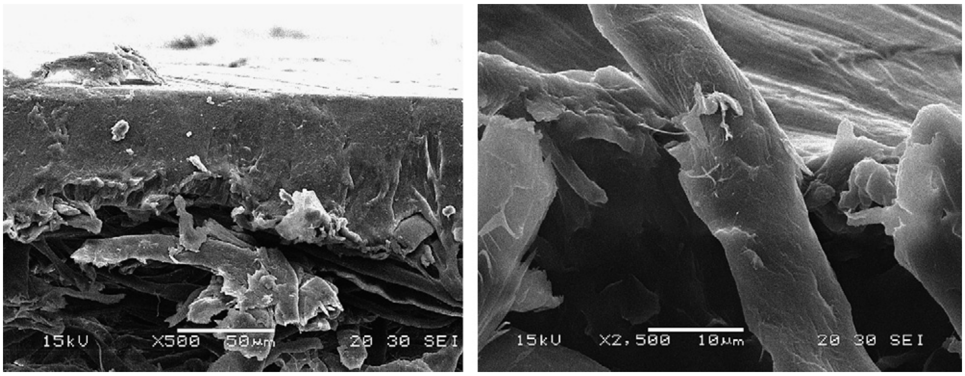

Fig. 10. SEM of fracture surfaces of the acetylated cellulose cardboard/PHB composite.

seen that the fiber of cellulose is covered by the layer of matrix material that had been pulled out together with the fiber. This is also a clear indication that the acetylated cellulose has an effective interaction with PHB.

4. Conclusions

It was possible to obtain a novel bilayer films using different amount of polyhydroxybutyrate (PHB) and cellulose cardboard. The materials were made by compression molding of a film of PHB and a sheet of cardboard.

Cellulose cardboard coated with PHB can be development to fabricated cardboard based food packaging material, with superior barrier and mechanical properties than the cardboard alone.

In addition, these bilayer materials are totally biodegradable with very useful properties and low cost.

Cardboard coated with PHB showed several interesting characteristics. All bilayer composites showed improved permeation properties. As of 15% of PHB, water permeation, equilibrium moisture content and polarity showed a marked drop. It is therefore assumed that the hydrophobic PHB covered up the cellulose cardboard and formed a continuous layer.

The elastic modulus (E), tensile strength (σ) and strain at break (ε) of bilayer biocomposites depend on the PHB content but did not follow the rule of mixtures. Improved uniaxial tensile behavior was obtained in composites with more than 15% of PHB. If the samples were conditioned, the elastic module was less and the elongations at break were higher than the dry samples. This effect is due to the effect of water incorporated to the cellulose that produces more relative motion between the fibers in the zone of the cardboard.

The bilayer composites with acetylated cellulose cardboard showed better adhesion and less absorption of humidity than the PHB/cellulose cardboard composites, due to diminish of hydrophilic character of cellulose and then superior compatibility with the PHB. The degree of treatment can affect the mechanical properties of composites significantly.

It was demonstrated that two-layer PHB-cellulose films exhibited suitable barrier and mechanical performance for packaging applications, taking advantage of the good properties of both of them.

Acknowledgments

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