

Biodegradable Double-Layer Films Based on Biological Resources: Polyhydroxybutyrate and Cellulose

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ABSTRACT: A novel biocomposites double-layer films using polyhydroxybutyrate (PHB) and cellulose paper were produced. The biocomposites were prepared by the solvent-casting method (with chloroform). Films of the blends were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron micrograph (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray (XR) and surface roughness measurements. Moisture absorption, water absorption and water vapor permeation of films has been investigated. The PHB impregnated the fibers of cellulose paper and it was on the valley of paper structure. The double-layer films showed diminutions in the moisture absorption, in the water absorption, in water vapor permeation and in surface roughness. According to contact angle, surface free energies and the

barrier properties of the films can be considered more hydrophobic. The experimentally observed tensile properties (modulus and tensile strength) of double-layer films with different content of PHB were determined. Measurements show the tensile strength and modulus of cellulose paper increases with the percentage of PHB. SEM photomicrographs of the fractured films surfaces were also analyzed. It was possible to obtain a biodegradable material with little amount of PHB to improve the barrier and the mechanical properties of cellulose paper, taking advantage of the good properties of both materials. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 749–756, 2007

Key words: polyhydroxybutyrate; cellulose; biodegradable composites

INTRODUCTION

Plastics are used in many applications such as in packaging, structure materials, and commodities as well as in cleanliness products. These materials are widely used in food packaging applications due to their capability to control the mass exchange of low molecular weight compounds between the food and its exterior environment. It is really important to assure the correct shelf-life of the packed product. Actually, one of the most serious environmental concerns is the amount of waste produced and accumulated. Biodegradable films based on biopolymers have been developed as attractive solutions to significant environmental problems.^{1,2}

Polyhydroxyalkanoates (PHAs), of which poly(hydroxybutyrate) (PHB) is the most common, are carbon energy storage materials produced by numerous

bacterial species. PHAs are now under intensive investigation because of its inherent property as a biodegradable thermoplastic. PHB is biodegradable polyester, semicrystalline thermoplastic and hydrophobic polymer. A very interesting property of PHB with respect to food packaging applications is its low water vapor permeability, which is close to that low-density polyethylene. However, they are still expensive and quite brittle.^{3–5}

Cellulose is the primary product of photosynthesis and it is abundant renewable bioresource. Cellulose is a linear polymer of (β-1,4)-D-glucopyranose units. Cellulose forms crystals where intramolecular and intrastrand hydrogen bond holds the network flat allowing the more hydrophobic ribbon faces to stack. The water molecules catalyze the formation of natural cellulose crystals by aligning chains through hydrogen-bonded bridging. Another part of cellulose is amorphous and is found between these crystalline sections. The overall structure is of aggregate particles with extensive pores capable of holding relatively large amounts of water capillarity. The only widely used renewable packaging materials are paper and cardboard, which are based on cellulose, the most abundant renewable polymer worldwide. Paper has excellent mechanical properties, but the

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vapor permeability is too high for many applications. The hydrophilic nature of the paper-based materials is a major problem of these materials when packaging moist foods.⁶

Many research and industrial efforts have been made to use PHB for a variety of purposes. However, the high production cost of PHB has prohibited its application as "plastic." In addition, the PHB films are typically brittle, which may limit their applications in situations that require high tensile strength. Therefore, materials with better mechanical properties and less cost can be prepared by compounding the bioplastic with natural fibers or with other polymers.

The water vapor permeability of polymers is an important characteristic when they are used as protective coatings for insulating and packaging materials. Data on the swelling, diffusion, and permeability of polymers are needed for the selection of the materials and for predicting the service life in humidity media. 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.^{7,8}

The aim of this work was to determine the barrier and mechanical properties of a fully biodegradable double-layer composites using polyhydroxybutyrate and cellulose paper. The use a thin layer of PHB to coat the paper-based materials offers interesting possibilities to prepare less expensive biodegradable materials with useful properties. PHB, as a semicrystalline and hydrophobic polymer, may therefore protect cellulose paper from moisture sensitivity. Effects of content of PHB on the final properties of the biocomposites will be analyzed.

EXPERIMENTAL

Materials

A biodegradable polymer, polyhydroxybutyrate (PHB) ($M_n = 42,500$) was used, kindly supplied by PHB Industrial S.A., Brazil. Cellulose paper of jute from Celesa Celulosa de Levante S.A., was also used.

Preparation of the double-layer films

The biocomposites of PHB and cellulose paper with different amounts of PHB (2, 5, 10, and 15 wt %) were obtained by a solvent-casting method using chloroform as a solvent. The homogeneous solutions of PHB with chloroform were prepared at 60°C for the shortest time possible: 15 min, to avoid the thermal degradation of the PHB. This solution was poured into petri dishes, onto cellulose paper and kept at room temperature for 24 h to permit gradual evaporation of the solvent. The resultant double-

layer films were dried under vacuum to remove the all of the solvent. The dried films were stored at room temperature for fifteen days in order to allow the complete crystallization of the PHB. The top side of the composites consisted of PHB, and the bottom side of the composites was cellulose paper.

Characterizations: Testing of films

Thermal gravimetric analysis was performed on the samples with a Mettler TA 4000 at a heating rate of 10°C/min under a nitrogen atmosphere. The sample weight was between 3 and 7 mg.

The infrared spectra of the composites on the top and bottom sides were obtained by Infrared Spectroscopy with the Fourier Transformed technique (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 CH₂ groups; which is insensitive to the composition and degree of crystallinity.⁹

X-ray diffractograms were obtained with KCu α ($\lambda = 1.54 \text{ \AA}$) radiation in a Philips PW 1710 X-ray diffractometer system. The X-ray tube was operated at 45 kV and 30 mA, at 2° min⁻¹.

The DSC analysis of composites was determined using a Perkin Elmer Pyris 1. The dry and conditioned (at 75% RH) samples were subject to the heating scan between -40°C and 230°C to obtain a fusion temperature. The scanning rate was 10°C/min.

The surface roughness was measured in order to characterize the surfaces, using a Taylor-Hobson, subtronic 3+, precision: 2%. The length of measurement was 4mm with a resolution of 0.02 μm .

The contact angle determination was made by the sessile drop method. Drops of ethylene glycol (99.1% by Aldrich) and diiodomethane (99% by Aldrich) were formed on the surfaces of composites. The contact angles of the drops were measured between the liquid and the films with a MV-50 camera, 6 \times zoom and acquired with the NIH imaging software. The measurements were the average of 5 drops per liquid.

Water absorption tests were performed in a container of distilled water maintained at a 25°C (ASTM D570). The samples were dried in an oven for 24 h at 50°C, and immediately weighed and immersed in water. At different times the specimens were removed from the water, wiped off with a dry cloth, and weighed immediately. The dimensions of the specimens were 2.5 \times 3 cm. The samples were sealed with silicon on the bottom sides (without PHB), to prevent the entry of water from this side.

The constant relative humidity environment (RH) was generated with aqueous saturated salt solutions

(with NaCl), in a hermetic glass container, to obtain 75% RH (ASTM E 104-85). Before water absorption testing, the films of PHB, cellulose paper and composites were dried at 45°C until a constant weight (w_0). The samples were kept at 75% RH and the increasing weight was measured at different times (w_t).

Water vapor permeability tests were conducted using ASTM E 96-80 method 17. Each film sample was sealed over a circular opening of 0.00177 m² in a permeation cell that was stored at 25°C in desiccators. To maintain a 75% relative humidity (RH) gradient across the film, anhydrous silica (0% RH) was placed inside the cell and a saturated NaCl solution (75% RH) was used in the desiccators. The RH inside the cell was always lower than that outside, and water vapor transport was determined from the weight gain of the permeation cell. When steady-state conditions were reached (about 1 h), eight weight measurements were made over 5 h. Changes in the weight of the cell were recorded as a function of time with all the samples.

The mechanical properties of the composites (dry and conditioned at 75% RH samples) were determined with the INSTRON 4467 mechanical testing machine. Tensile testing of bone-shaped composite specimens was carried out using a crosshead rate of 2 mm/min (ASTM D 1708-93). The analysis of the fractured surfaces of the samples was performed by means of scanning electron microscopy (SEM), in order to observe the morphology of the composites.

RESULTS AND DISCUSSIONS

Thermal characterization of double-layer films

The results of the thermal gravimetric analysis of double-layer films, PHB films, and cellulose paper are shown in Figure 1. It can be observed that the

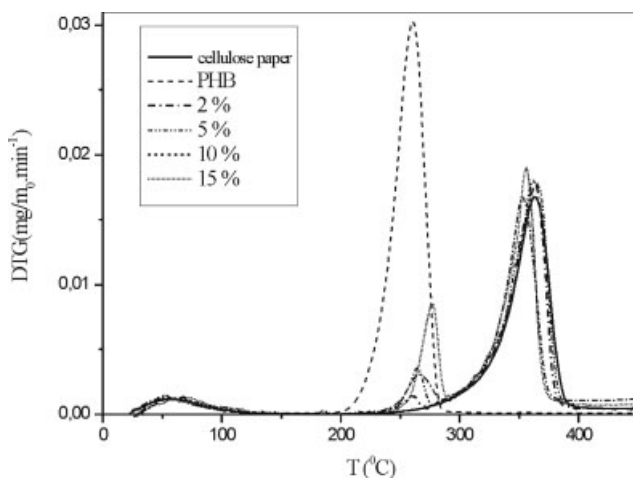


Figure 1 Dynamic thermal gravimetric analysis at a heating rate of 10°C/min of cellulose paper, PHB and the double-layer composites.

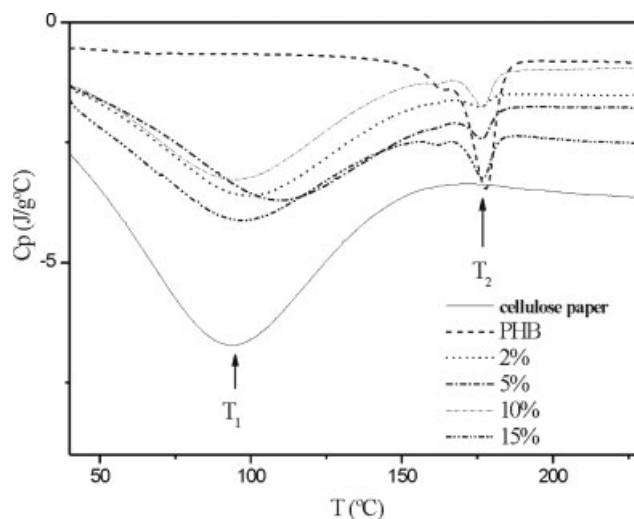


Figure 2 DSC runs for PHB, cellulose paper and their composite films.

degradation of the PHB is characterized by one peak at 261°C. The spectrum of the cellulose paper shows one peak at 364°C. The peak corresponding to the PHB in the films shifted to a higher temperature due to the interaction between the PHB and cellulose paper, which made PHB/cellulose paper more thermally stable and the PHB more difficult to degrade.

The recorded DSC curves obtained for the composites are shown in the Figure 2. The composites displayed two peaks: the single peak corresponds to the evaporation of the water content in cellulose paper and the double peak corresponds to the fusion of PHB.

Fourier transformed infrared spectroscopy

Figure 3 shows two regions of infrared spectra of PHB, cellulose paper, and the composites. In order

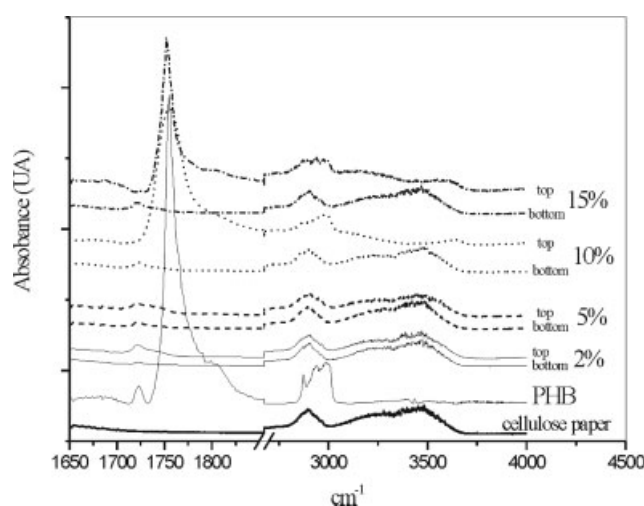


Figure 3 FTIR spectra of cellulose paper, PHB and composites. Normalized to 2933 cm⁻¹ peak height.

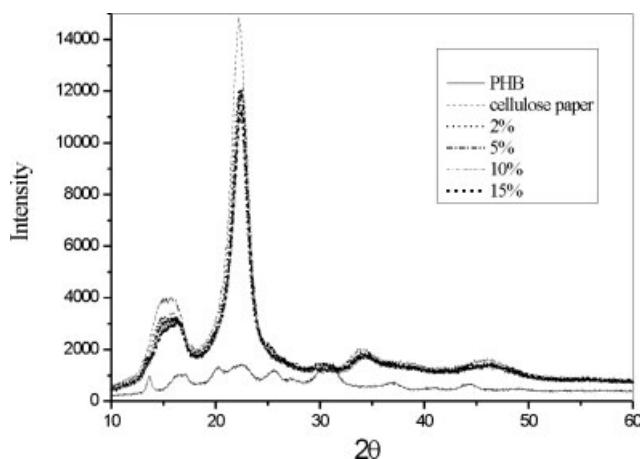


Figure 4 X-ray diffraction patterns for cellulose paper, PHB and their composite films.

to compare spectra of different samples, the area of the peaks was normalized to 1382 cm^{-1} ; this band corresponds to the stretching of CH_3 , which is insensitive to the composition and degree of crystallinity. As shown in the Figure 3, the absorption of the hydroxyl groups in cellulose paper is strong and broad at 3460 cm^{-1} . The PHB shows a peak at about 1753 cm^{-1} , which corresponds to the absorption of carbonyl groups of PHB. For the composites, the bottom side spectrum is similar to the spectrum of cellulose paper and the top side spectrum is identical to the spectrum of PHB if the content of PHB is equal to or more than 10 wt %. The top-side spectrum showed a PHB peak only for composites with PHB content more than 10 wt %, indicating that for a quantity less than 10 wt %, the paper absorbed the entire PHB compound.

X-ray diffraction of PHB, cellulose paper, and double-layer films

The X-Ray diffraction pattern of all samples is shown in Figure 4. The spectra showed the peak of cellulose paper and PHB. The X-ray patterns showed that the cellulose paper is more crystalline than the PHB.

TABLE I
Thickness and Roughness Parameters of the PHB, Cellulose Paper and Their Composites

Sample	Thickness (μm)	R_a	R_t	W_t
Cellulose paper	703.0 ± 28.3	4.30	30.90	34.37
Cellulose paper + 2% PHB	693.6 ± 44.4	4.66	34.83	31.07
Cellulose paper + 5% PHB	645.2 ± 44.0	4.58	31.03	35.87
Cellulose paper + 10% PHB	690.8 ± 46.0	4.37	26.73	34.37
Cellulose paper + 15% PHB	760.7 ± 41.8	2.08	16.37	29.63
PHB	50.8 ± 7.8	0.24	1.68	3.72

TABLE II
Surface Energy Components of Probe Liquids for Contact Angle Measurements¹¹

(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

Thickness

The average thickness results for the samples are shown in the Table I. The cellulose paper keeps the original thickness for all the samples except those with 15 wt % of PHB.

Surface free energy

The surface free energy parameters were calculated using the contact angle of the probe liquids. To determine the total surface energy of the materials and their polar and dispersive components, the Owens and Went equation was used:¹⁰

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

where 1 and 2 refer 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):

$$\gamma_1 = (\gamma_1^d + \gamma_1^p) \quad (2)$$

The surface energy components of probe liquids used for the contact angle measurements are listed in Table II. Ethylene glycol (polar liquid) and diiodomethane (apolar liquid) was used to measure the contact angle.

The polar and dispersive components of the surface energy calculated are shown in the Table III for the PHB and cellulose paper with 15 wt % of PHB. A diminution of the dispersive component was observed, as well as an increment in the polar component of the surface energy with the addition of

TABLE III
Surface Energy Components and Polarity of Films of PHB and Cellulose Paper 15% of PHB

Sample	γ_d	γ_p	γ	x^p
PHB	37.941	1.049	38.99	0.02690433
Cellulose paper + 15% PHB	32.359	7.173	39.532	0.18144794

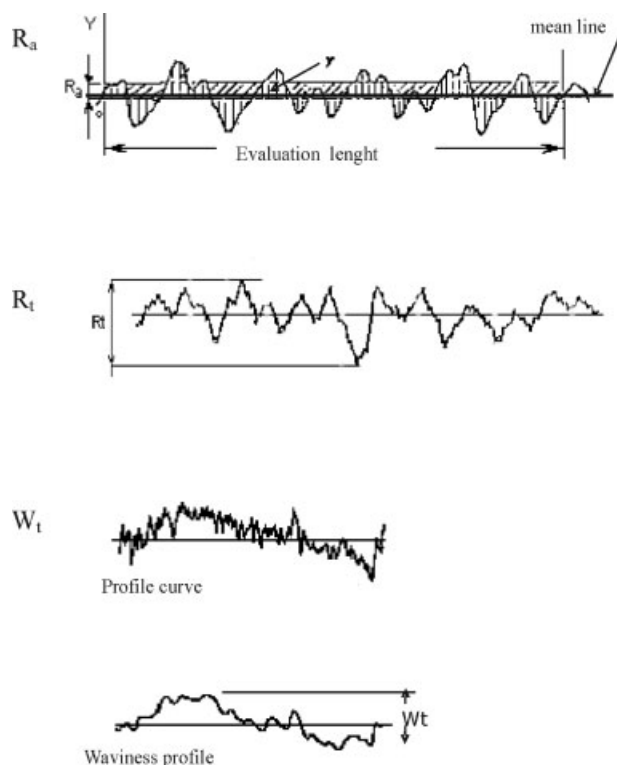


Figure 5 Determination of the parameters of surface roughness.

PHB to the cellulose paper, because the hydrophilicity of the cellulose. In Table III is also shown the polarity of different films, x^p , defined as

$$x_p = (\gamma^p/\gamma) \quad (3)$$

It was impossible to measure the contact angle for lower wt % of PHB than 15 wt % because the drop was absorbed for the sample. This indicates that the PHB was impregnated and it is in the "valley" of the structure of paper.

Surface roughness

Surface roughness is of great importance in many areas because it highly affects the function of surface.¹²

Three roughness parameters: arithmetical mean roughness (R_a), maximum peak-to-valley height (R_t), and waviness (W_t) were obtained to evaluate the roughness of the composites. Figure 5 shows how these parameters are defined.

R_a is the arithmetic mean of the absolute values of the departures of the profile from the mean line. R_t is the distance between the maximum peak height and the maximum valley depth. W_t is the distance between the maximum peak height and the maximum valley depth of the curves obtained by removing the

short wavelength components (roughness components), thus obtaining a filtered waviness profile.

Table I shows average values of the three roughness parameters taken from the surface of the samples.

The roughness of the composites with less of 15 wt % is similar to the roughness of cellulose paper. This indicated that the PHB is inside of the cellulose paper. The composite with 15 wt % of PHB showed low roughness parameters because this quantity of PHB is enough to occupy the valley of the structure of cellulose paper, and made surfaces smoother.

Morphology

Figure 6 shows the micrographs obtained by SEM of the cellulose paper, the PHB, and of composites with different amounts of PHB. In all composites analyzed, there is one zone with higher density which corresponds to PHB, one interfacial zone with cellulose fiber and PHB and another zone which correspond to cellulose paper.

Equilibrium moisture content

The moisture content as a function of time was determined in order to measure the equilibrium moisture content of films of PHB, cellulose paper, and double-layer composites. Figure 7 shows the percentage increase in weight value ($w\%$) of the samples, at 25°C. The percentage increase in weight value ($w\%$) was calculated as follows:

$$w\% = \frac{w_t - w_0}{w_0} \times 100 \quad (4)$$

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

Table IV shows the equilibrium moisture content average of the samples. The films of PHB absorb less water than the cellulose paper as a consequence of lower hydrophilicity. The PHB produces a decrease in the maximum moisture absorption because: (1) the PHB is in the pores of the cellulose paper and prevents the entry of water and (2) PHB is less hydrophilic than cellulose paper.

Water absorption value

Percentage increase in weight during immersion was calculated as follows:

$$w_{in} \% = \frac{w_{in t} - w_{in 0}}{w_{in 0}} \times 100 \quad (5)$$

where, $w_{in t}$ is a wet weight of samples at each time; $w_{in 0}$ is the initial weight of dry samples.

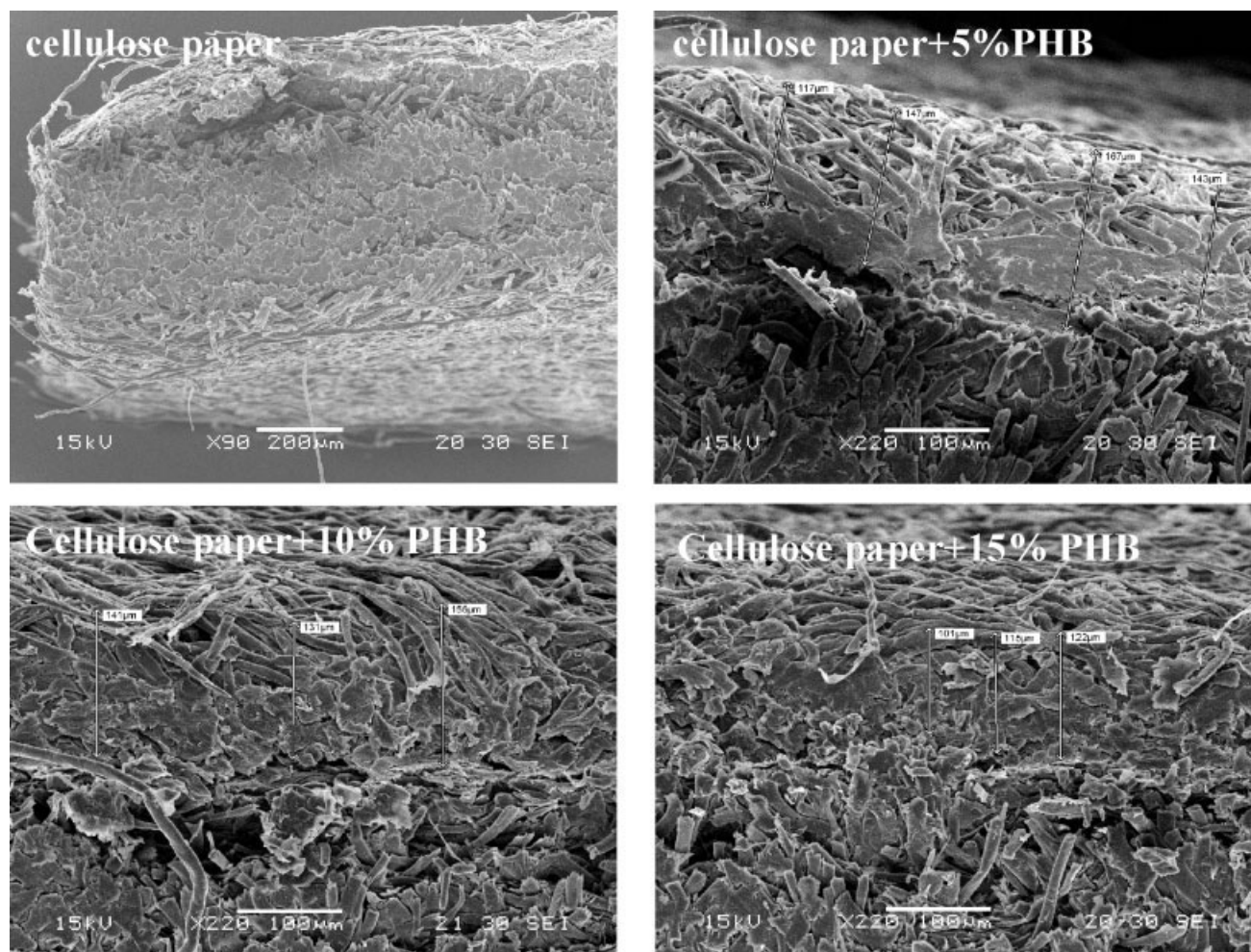


Figure 6 SEM of fracture surfaces of the composite.

The percentage of water absorbed (see Table IV) decreased with the content of PHB. Again, this is because the PHB is more hydrophobic than the cel-

lulose paper, and because the surface fibers on the cellulose paper were covered with the PHB.

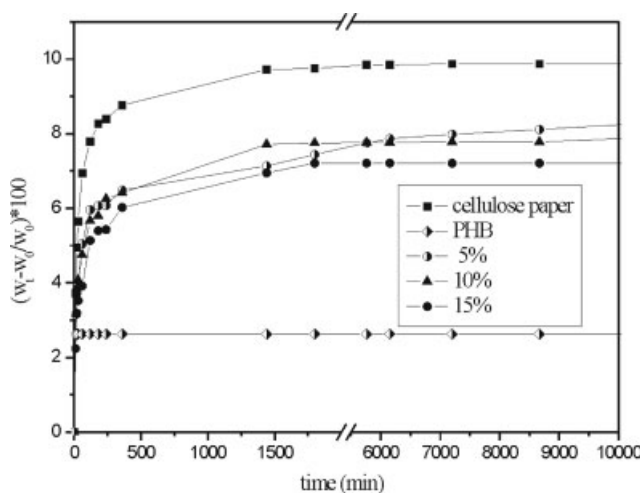


Figure 7 Percentage increase in weight value (wt %) at 75% HR of: cellulose paper, PHB and composite films.

Water Vapor Permeation

Changes in the weight of the cell were recorded and plotted as a function of time. The slope of each line was calculated by linear regression, and the water vapor transmission rate (WVTR) was calculated from the slope (g/s) divided by the cell area (m^2). Water vapor permeation (WVP) ($g/Pa s m$) was cal-

TABLE IV
Equilibrium Moisture Content (w_{∞}) and Equilibrium Water Content ($W_{in \infty}$) for Cellulose Paper and Composite Films

Sample	w_{∞} (%)	$W_{in \infty}$ (%)
Cellulose paper	9.8 ± 0.3	430.2 ± 50.6
Cellulose paper + 2% PHB	8.4 ± 0.5	
Cellulose paper + 5% PHB	8.1 ± 0.2	139.2 ± 14.2
Cellulose paper + 10% PHB	7.4 ± 0.2	82.5 ± 7.9
Cellulose paper + 15% PHB	2.6 ± 0.2	71.4 ± 3.7

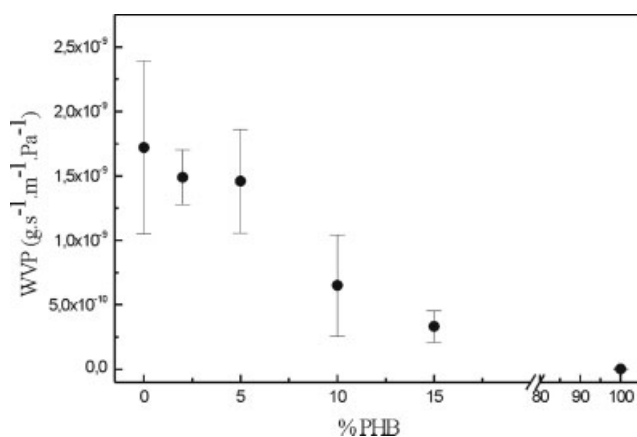


Figure 8 WVP of cellulose paper, PHB and composite films.

culated as

$$\text{WVP} = \left[\frac{\text{WVTR}}{S(R_1 - R_2)} \right] d \quad (6)$$

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 six sampling units taken from different films.

Figure 8 shows the effect of different amounts of PHB on the WVP of composites with cellulose paper. The films of PHB present a lower value of WVP than that of the cellulose paper. The permeation of the composites decreased with the amounts of PHB due to the low permeation of PHB. However, it is necessary for the PHB to form a continuous layer above the cellulose paper in order to be efficient. If

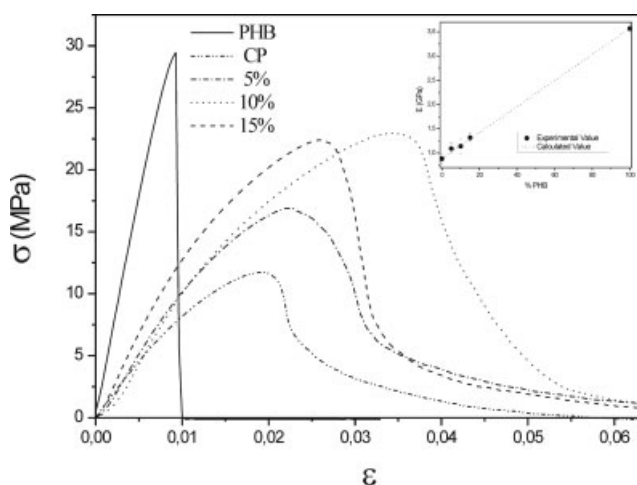


Figure 9 Tensile test results for the cellulose paper, PHB and composite films and experimental values of Young's modulus and calculated values.

TABLE V
Results of the Tensile Testing of the Cellulose Paper, PHB, and Composites with Different PHB Content

Sample	E (GPa)	σ (MPa)	ϵ (%)
Cellulose paper	0.88 ± 0.12	11.7 ± 2.4	18.3 ± 2.6
Cellulose paper + 5% PHB	1.09 ± 0.13	17.7 ± 1.8	22.9 ± 1.3
Cellulose paper + 10% PHB	1.14 ± 0.15	23.7 ± 1.3	36.4 ± 4.3
Cellulose paper + 15% PHB	1.32 ± 0.09	22.9 ± 2.0	29.1 ± 3.2
PHB	3.57 ± 0.10	28.9 ± 0.7	10.2 ± 1.2

the amounts of PHB are not sufficient to fill all of the valleys of the cellulose paper's structure, water vapor permeates through the cellulose paper.

Mechanical properties of PHB, cellulose paper and double-layer films

Tensile tests were performed on the PHB, the cellulose paper and the double-layer films. The stress-strain curves of these films are shown in Figure 9. In

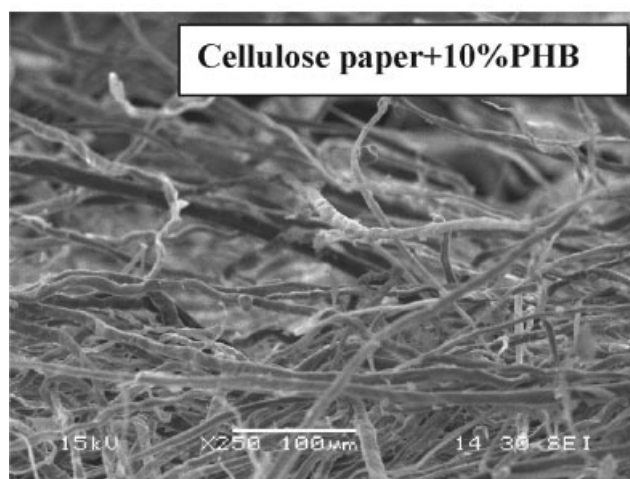
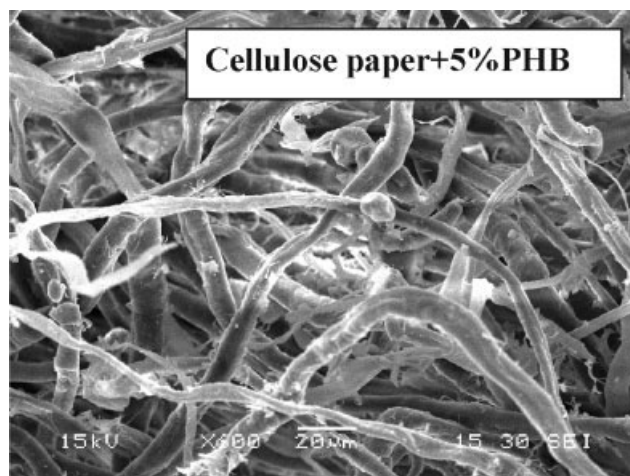


Figure 10 SEM of fracture surfaces of the composite.

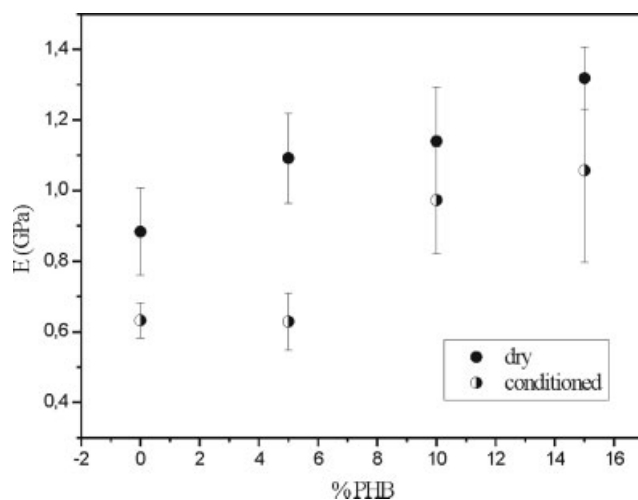


Figure 11 Modulus of conditioned samples and dry samples.

Figure 9 we can see that PHB is a fragile material with a relatively high modulus (3.57 GPa), and the cellulose paper shows a delaminating behavior with a lower modulus (0.88 GPa). The values of the elastic modulus, stress, and strain at break obtained for the double-layer composites are reported in Table V. The modulus, stress, and strain at break increase with the increase of the content of PHB. The composites show stress-strain curves similar to those of cellulose paper, when pulling the cellulose fiber, but at higher stress values, because the interface fiber (cellulose paper)-PHB resists the applied force.

Young modulus can be calculated from the rule of mixture as follow:

$$E_c = w_1 E_1 + w_2 E_2 \quad (7)$$

where E_1 is the modulus of PHB, E_2 is the CP modulus and w_1 is the PHB mass fraction and w_2 is the CP mass fraction.

The experimental values of Young's modulus agree with the calculated values, as can be seen in Figure 9(b).

The observation by SEM of the fracture surface of the composites, reported in Figure 10, confirms the pulling out of fibers from the cellulose paper.

Tensile tests were performed on the PHB, the cellulose paper and the double-layer films conditioned at 75% HR. The values of the elastic modulus obtained for the double-layer composites dry and conditioned are reported in Figure 11. The conditioned composites show a lower modulus than the

dry samples due to the plasticizer effect of water on cellulose paper fibers.

CONCLUSIONS

Double-layer biocomposites based on PHB and cellulose paper have been investigated. In order to find the best properties, the PHB influence on cellulose paper was studied.

A diminution in the moisture and water absorption as well as in water vapor permeation and surface roughness was observed in the double-layer films, compared to cellulose paper. The PHB impregnated the fibers of the paper and occupied the valleys in the paper's structure; in consequence, the cellulose paper had less free volume and hydrophilicity, with less affinity to the molecules of water.

It was found that the elastic modulus and mechanical strength of the composites increase with PHB content. The experimental data agreed greatly with the mixing rule law predictions.

The enhancement in the properties was obtained when more than 10 wt % of PHB was added to cellulose paper.

The relationship among the different properties analyzed leads to useful conclusions regarding the possible future uses of the films. This method offers one interesting possibility to prepare less expensive biodegradable materials with good properties using a cellulose paper coated by a thin layer of PHB.

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