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Xylan–cellulose films: Improvement of hydrophobicity, thermal and mechanical properties

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ABSTRACT

Xylan-rich hemicellulose from corn cob has been used for new material elaboration. Commercial cellulose was used as reinforcement in different percentages to improve properties of the films. Two types of composites were elaborated by solvent casting. *Hydrophilic films*, composed by bleached hemicellulose (BH), unmodified cellulose and glycerol as plasticizer, and *hydrophobic films* formed by acetylated bleached hemicellulose (BAH) and acetylated cellulose. The degree of substitution of BAH was 1.8 and acetylated cellulose presented a degree of substitution of 0.54. Thermal and mechanical properties of films were analyzed. A significant improvement was observed in the thermal behavior of hydrophobic films (T_{max} ~ 368 °C) respect to hydrophilic films (T_{max} ~ 300 °C). Although the addition of cellulose clearly increase the properties of both type of films, hydrophobic films (Young's modulus ~2300 MPa, strength ~44.1 MPa, strain at break ~5.7%) showed better mechanical properties than hydrophilic films (Young's modulus ~3 MPa, strength ~3.3 MPa, strain at break ~5.3%).

1. Introduction

Nowadays, most plastics materials produced are from petroleum. Although the development of polymeric materials has a vital importance in the society over the years and has contributed to facilitate our way of life, their use creates many potential problems due to their non-renewable nature and ultimate disposal (Saxena & Ragauskas, 2009). Moreover, the plastics are present in most products consumed and used every day, is a material used in all industrial sectors and for the manufacture of a wide range of products. Therefore, in recent years, the growing environmental concerns have created an urgent need to develop biodegradable materials that have comparable properties to polymeric materials at an equivalent cost. For this purpose, the use of lignocelluloses resources as agricultural wastes, are becoming an attractive alternative due to their renewable origin, the biodegradability of their components and their non-human food application (Mikkonen & Tenkanen, 2012). In addition, agricultural residues are produced in large quantities every year and most of them being discarded and burned with no value. Hemicelluloses, the second most abundant biopolymer on Earth has a great potential as bio-based and biodegradable packaging materials (Mikkonen et al., 2011; Stepan, Höije, Schols, De Waard, & Gatenholm, 2012), constitute about 20–35% of most plant depending on the particular plant species (Ayoub, Venditti, Pawlak, Sadeghifar, & Salam, 2013; Fang, Sun, Tomkinson, & Fowler, 2000). Its structure is amorphous in nature and can be formed by a wide variety of monosaccharides including: xylose, arabinose, glucose, galactose, mannose, fructose, glucuronic acid and galacturonic acid depending upon the source (Stepan et al., 2012; Ayoub et al., 2013) and used extraction method. Xylans are an important sub-group of hemicelluloses with a β(1-4)-D-xylopyranose backbone with various ramifications and substitutions. They are found mainly in hardwoods, and agricultural plant species (Hansen, Blomfeldt, Hedenqvist, & Plackett, 2012; Peng, Ren, Zhong, & Sun, 2011). Hemicelluloses are hydrophilic molecules and have good barrier properties against oils and fats, but are less efficient as moisture, and water vapour barriers. Also, oxygen barrier properties are good at low or moderate relative humidities, particularly for xylans (Gröndahl & Gatenholm, 2007; Tharanathan, 2003). However, synthetic polymers are usually hydrophobic, and this significantly limits the use of hemicellulose in industrial applications. However, due to the reactive groups (hydroxyl groups), hemicelluloses properties can be modified by different reactions. Many authors have studied chemical treatments of the hemicelluloses with the aim of substitute the hydroxyl group of hemicellulose to increase material hydrophobicity and thermal stability of modified hemicellulose (Belmokaddem, Pinel, Huber, Petit-Conil, & Da Silva Perez, 2011; Grace, Fundador, Enomoto-Rogers, Takemura, &

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Iwata, 2012; Jonoobi et al., 2012). Hemicellulose based composite materials have also been developed in an attempt to improve the hemicellulose material properties because mechanical properties of pure hemicellulose-based films are generally considered being low without additives (Stevanic, Bergstrom, Gatenholm, Berglund, & Salmén, 2012). Therefore, in recent years, incorporation of biodegradable reinforcements such as cellulose into other polymers has already proven to be an important strategy for obtaining composites with high mechanical performance. These biodegradable reinforcements also offer great possibilities for the development of novel hemicellulose-based composite materials and its structure allows surface modification to improve compatibility with hydrophobic matrix. Several publications can be found about the use of hemicelluloses reinforced with cellulose for materials productions (Mikkonen et al., 2012; Stevanic et al., 2011) and the use of modified cellulose as reinforcement in hydrophobic matrix such a poly(lactic acid) in order to improve compatibility between two components in new material (Lin, Huang, Chang, Feng, & Yu, 2011; Tingaut, Zimmermann, & Lopez-Suevos, 2010). The present study was focused on hemicellulose extraction from a renewable resource and purification for elaboration new materials. The main effort has been to evaluate the initial hemicellulose film characteristics and the improvement of its thermal and mechanical properties through the addition of cellulosic reinforcement in different percentages and use acetylation process. Hemicellulose was acetylated in order to obtain hydrophobic matrix and also for greater thermal stability. Commercial cellulose was also acetylated to improve affinity with hydrophobic matrix and so improve mechanical properties of hydrophobic films. The object of this research was to evaluate physical, thermal and mechanical properties of two types of elaborated biocomposite films and the effect of modified cellulose addition.

2. Materials and methods

2.1. Hemicellulose extraction, purification and acetylation

Hemicelluloses used for composites elaboration has been extracted from corn cob, was purified by ultrafiltration and then subjected to a bleaching process (BH) following the same method described by Egüés et al. (2014). The acetylation treatment was performed with the aim of substitute the hydroxyl group of hemicellulose and increase material hydrophobicity (BAH). Acetylation process was also the same as followed by Egüés et al. (2014).

2.2. Cellulose: characteristics and acetylation

Commercial cellulose nanofibers used in this work were provided by the University of Maine, Orono, United States. The average size is 100–200 nm lengths and diameters of between 10 and 20 nm. Cellulose acetylation was carried out using similar process to that used to acetylate the hemicellulose but with some modification. 0.5 g of nanofibers was dispersed in 25 mL formamide under vigorous stirring at room temperature until a homogeneous phase was obtained. Then, 40 mL pyridine was added. Every 3 h, 3.3 mL of acetic acid anhydride was added until a total of three additions. 25 h later, the viscous dark solutions were thrown into 1 L of distilled water. Acetylated cellulose was filtered and washed with acetone, followed by ethanol and distilled water until neutral pH. This washing step allowed the removal of unreacted acetic acid and pyridine from the samples. The acetylated cellulose was dried in an oven at 50 °C for further characterization.

2.3. Films elaboration

Two types of composites have been prepared; one was formed by bleached hemicellulose (BH) reinforced with unmodified cellulose (*hydrophilic films*). In this case, glycerol was used to obtain a continuous film. The second type was formed of acetylated hemicellulose (BAH) as matrix and acetylated cellulose as reinforcement (*hydrophobic film*). Both films have been elaborated by solvent casting. In both cases, three steps were necessary in order to produce homogenous films. For hydrophilic films elaboration; (a) bleached hemicellulose solubilized in 10 mL of water for about 3 h, (b) cellulose was dispersed during 3 h in 10 mL distilled water with magnetic stirring (c) finally, solubilized hemicellulose was added to dispersed cellulose, and last glycerol was added and stirred for 1 h. The total amount of dry substance (hemicellulose and cellulose) in each film was kept constant at 0.5 g. The cellulose content in the composite films was 0, 1, 5, 10 and 20.0 wt% of the total dry mixture, respectively. The glycerol content was kept 40 wt% (based on the total dry mixture). The solutions were poured onto polystyrene dishes (9 × 9 cm) and allowed to dry at 25 °C and 50% RH in a climate-controlled chamber for 7 days. For hydrophobic film, chloroform was used as solvent for its ability to dissolve acetylated hemicellulose and disperse acetylated cellulose; (a) acetylated cellulose was dispersed at room temperature with magnetic stirring in 10 mL of chloroform for 2–3 h, then sonicated for about 5–10 min, (b) acetylated hemicellulose solubilized in 10 mL of chloroform for about 3 h and finally, (c) solubilized hemicellulose was added to the dispersed cellulose and stirred in order to form a homogeneous solution. The total amount of dry substance (hemicellulose and cellulose, both acetylated) in each film was also kept constantly at 0.5 g. The cellulose content in this case was 0, 1 and 5% of the total dry mixture. After completing the process of obtaining films, the solutions were poured onto polystyrene dishes (9 × 9 cm) and were dried in a vacuum oven (500 mBa) at 30 °C in order to avoid the occurrence of bubbles in the films. All composites were conditioned prior to analysis at 25 °C and 50% relative humidity in a climate-controlled chamber.

3. Characterization

The weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (IP = M_w/M_n) of the bleached hemicellulose was determined by gel permeation chromatography (GPC) in a GPC Jasco LC-Net II/ADC equipped with a photodiode array detector and refractive index detector. The column was PL aquagel-OH MIXED. The mobile phase was constituted by 0.005 N H_2SO_4 prepared with 100% deionised and degassed water (0.6 mL/min flow, 40 °C and injection volume of 40 μL). Calibration curve was made using Pullulan polysaccharides (Calibration kit SAC-10, Varian) with different molecular weights (between 180 and 805,000 Da).

Sugars monomers quantification was carried out in a high performance liquid chromatography (HPLC) Jasco LC Net II/ADC equipped with a refractive index detector and a photodiode array detector. A Phenomenex Rezex ROA HPLC column with 0.005 N H_2SO_4 prepared with HPLC grade degassed water was used as mobile phase (0.35 mL/min flow, 40 °C and injection volume 40 μL). High purity standards of D (+) glucose, D (+) xylose, D (−) arabinose, galacturonic acid, and acetic acid (supplied by Sigma–Aldrich), were used for the calibration curves. For monomeric sugars quantifications, bleached hemicellulose (BH) samples were subject to post-hydrolysis process, using sulphuric acid at a concentration of 4% (w/w) for 60 min.

The FT-IR analysis of dried samples of acetylated and nonacetylated cellulose was performed on a NICOLET MODEL NEXUS 670 FT-IR spectrophotometer. Acetylated and bleached hemicellulose

was also analyzed. All samples were analyzed in order to confirm that the acetylation reaction has been occurred successfully. A total of 20 scans were accumulated in transmission mode with a resolution of 4 cm^{-1}. The spectrum was obtained from a range of 4000–650 cm^{-1}.

The degree of acetylation of acetylated hemicellulose (BAH) was calculated by ^{1}H NMR spectrometry, using a Bruker 500 MHz spectrometer at a frequency of 250 MHz with an acquisition time of 0.011 s, at room temperature. The spectrum was recorded over 32 scans and DMSO-d_6 was used as solvent for acetylated bleached hemicellulose (BAH).

The chemical degree of substitution (DS) is the average value of $-COCH_3$ groups that replace hydroxyls in every glucose cycle. The DS of the acetylated samples were determined through a saponification reaction (ASTM D 871-96). Approximately 0.5 g of dry acetylated cellulose was placed in a flask, and 8 mL of 75% ethanol was added. Then, the mixture was heated for 30 min at 60 °C. Following this, 8 mL of a 0.5 N sodium hydroxide (NaOH) solution was added, and the mixture was heated at 60 °C for 15 min. The flask was stoppered tightly and left to stand at room temperature for 72 h. Then, the NaOH was titrated with 0.5 N hydrochloric acid (HCl) with phenolphthalein as an indicator. At the point where the indicating pink color disappeared, an excess 1 mL of 0.5 N HCl was added, and the mixture was allowed to stand overnight. The small excess of acid was then back-titrated with a 0.5 N NaOH solution to the phenolphthalein end point (when the pink color reappeared). Blank titration was also performed with unmodified MFC, and the data was used as a reference. The acetyl content was calculated with the following equation:

$$\text{Acetyl content}(\%) = [(D - C)N_a + (A - B)N_b] \times \left(\frac{4.035}{W}\right) \quad (1)$$

where A is the volume of NaOH added to the sample (mL), B is the volume of NaOH added to the blank (mL), C is the volume of HCl added to the sample (mL), D is the volume of HCl added to the blank (mL), W is the weight of the sample (g), and N_a and N_b are the normality of the HCl and NaOH solutions, respectively. The average number of acetyl groups per anhydro-D-glucose unit of cellulose (DS) could be calculated from the following equation:

$$\text{DS} = \frac{3.86 \times \text{Acetyl content}(\%)}{102.4 - \text{Acetyl content}(\%)} \quad (2)$$

The X-ray powder diffraction patterns were collected by using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta–theta configuration, secondary monochromator with Cu–Ka radiation (λ = 1.5418 Å) and a PIXcel solid state detector (active length in 2θ 3.347°). The samples were mounted on a zero background silicon wafer fixed in a generic sample holder. Data was collected from 5° to 32° 2θ (step size = 0.026 and time per step = 80 s) at RT. A fixed divergence and antiscattering slit giving a constant volume of sample illumination were used. The crystalline index of cellulose, C_{Ir}, was calculated based on the empirical method proposed by Segal, Creely, Martin and Conrad (1959) where I_{200} is the peak intensity corresponding to cellulose I, and I_{am} is the peak intensity of the amorphous fraction.

$$C_{Ir}(\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (3)$$

Contact angle measurements were also carried out with water using a Dataphysics Contact angle system OCA 20, in order to determine changes in the hydrophilic character of cellulose after acetylation treatment. The average value of five measurements was calculated.

Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER TOLEDO. Cellulose, bleached hemicellulose and acetylated samples were analyzed to determinate their thermal stability. Samples about 5–10 mg were tested under nitrogen atmosphere at heating rate of 10 °C/min from 25 °C to 600 °C. Both types of composites were also analyzed to determinate their thermal stability.

Samples with 6 cm long were prepared, with thicknesses between 80 and 120 μm, and width of 5 mm, were mechanically tested by MTS Insight 10 equipment provided with pneumatic clamps (Advantage Pneumatic Grips) and with a loading cell of 250 N with a speed of 5 mm/min. The stress/strain measurements were performed using a video extensometer with digital video camera connected to a PC. The starting distance between the clamps was 25 mm. The values quoted are the average of eight measurements.

4. Results and discussion

4.1. Composition and GPC results of bleached hemicellulose

The composition of the bleached hemicellulose obtained after 60 min of post-hydrolysis and the average molecular weights are shown in Table 1. Obtained hemicellulose is composed mainly for xylose, galacturonic and small amount of arabinose and glucose. On the other hand, this sample had a high polydispersity because it has two fractions, one fraction with low molecular weight, about 20% of M_w = 3800 g/mol and the other 80% M_w = 67,300 g/mol.

4.2. FT-IR

Fourier transform infrared spectra of different samples are shown in Fig. 1. Both figures confirm that the acetylation reaction was successful. In the case of bleached hemicellulose (BH) (Fig. 1a) the bands found around 3400 and 2970–2830 cm^{-1} indicated the OH stretching and CH bond deformation of CH_2 and CH_3 groups, respectively. The other band found at 1630 cm^{-1} corresponds with water absorption (Ayoub et al., 2013). The absorbance between 1460 and 893 cm^{-1} seen in the spectrum is associated with native hemicelluloses (Sun, Fang, Tomkinson, & Jones, 1999). The presence of xylan was observed at 1035 cm^{-1} and the domain of β-glycosidic bonds between sugars units was demonstrated at 893 cm^{-1}. The evidence of acetylation was observed clearly in BAH, showed by the presence of three important ester bands (Ren, Peng, Zhong, Peng, & Sun, 2007; Sun et al., 1999) at 1735 cm^{-1} (C=O ester), at 1370 cm^{-1} ($-C-CH_3$) and at 1210 cm^{-1} (—C—O— stretching band). On the other hand, this analysis provides information about the chemical modification of cellulose fibers. Spectra in Fig. 1b showed 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 1735 cm^{-1}, this band is proceeding from wide C=O carbonyl peak from bonded acetyl group. In addition, a new absorption bands at 1370 cm^{-1} associated (C—H) the methyl in-plane bending and at 1230 cm^{-1}(C—O) was assigned to the carbonyl C—O stretch vibration (Lin, Huang, Chang, Feng, & Yu, 2011; Tingaut et al., 2010; Tomé et al., 2011).

4.3. Degree of substitution

The degree of substitution (DS) of the acetylation reaction was determined by ^{1}H NMR following the method used by Belmokaddem et al. (2011). The area of methyl protons of ester chains at 1.9–2.0 ppm (I_{methyl}) and the area of anomeric proton of xylan at 4.5 ppm ($I_{anomericXylan}$) were compared as shown in Eq. (4):

$$\text{DS} = \frac{I_{methyl}}{3 \times I_{anomericXylan}} \quad (4)$$

The spectrum in Fig. 2 showed the presence of an intense signal at 2.0 ppm, which was attributed to the acetyl moiety in the

Table 1
Sugar monomeric characterization and weight average (M_w), number average (M_n) and polydispersity index (M_w/M_n) of bleached hemicellulose.

	Xylose	Galacturonic Acid	Arabinose	Glucose	Ara/Xyl ratio	M_n	M_w	IP
BH	52.8	34.6	6.8	1.4	0.13	12,300	54,000	4.4

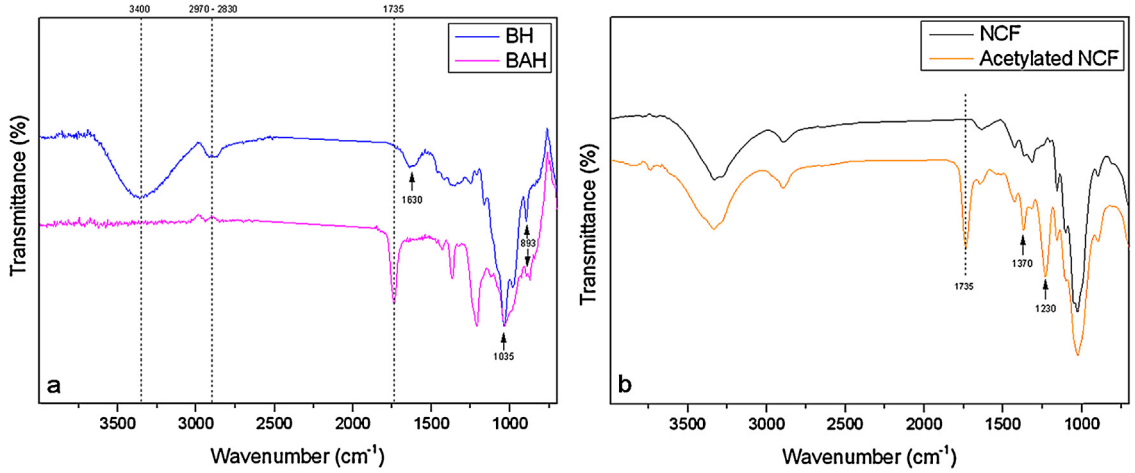

Fig. 1. Fourier transform infrared spectroscopy: (a) spectra of bleached hemicellulose (BH), bleached acetylated hemicellulose (BAH) and (b) spectra of nanocellulose fibers (NCF) and acetylated nanocellulose fibers.

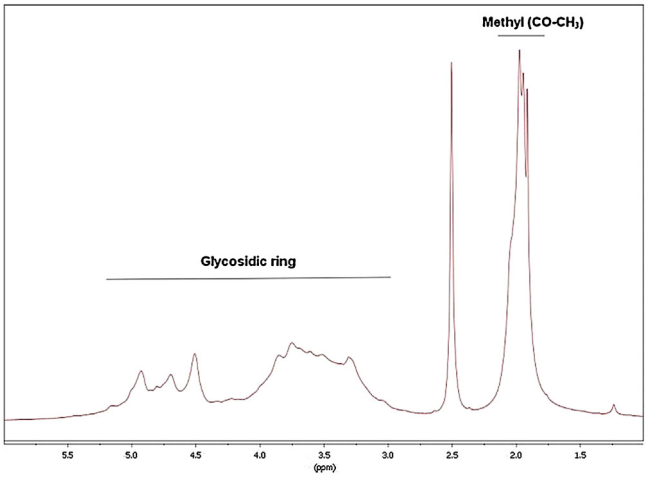

Fig. 2. ^{1}H NMR spectrum of bleached acetylated hemicellulose (BAH) (dissolved in DMSO-d6).

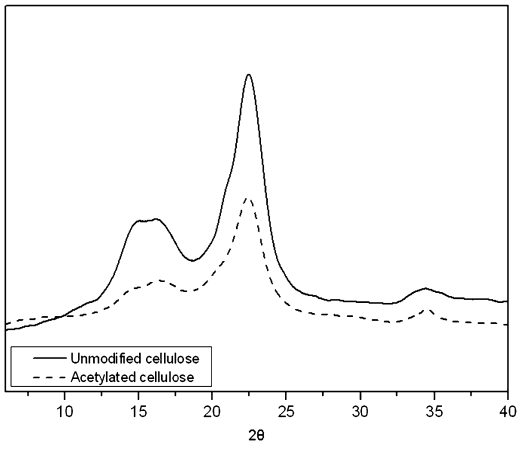

Fig. 3. XRD spectra of unmodified an acetylated cellulose fibers.

product, indicating that the acetyl groups were introduced into the hemicellulose molecules (Ayoub et al., 2013; Belmokaddem et al., 2011). In this study, the value of DS for bleached acetylated hemicellulose (BAH) was DS = 1.8. Taking into account that the average number of available OH groups per sugar unit is DS = 2, the degree obtained can be considered an acceptable value. In the case of cellulose, the acetyl contents determined by saponification were 12.6% after 30 h of reaction time. When Eq. (2) was applied, this could be translated to a (DS) of 0.54. Although the degree of substitution was not very high, it was adequate for correct dispersion of the fibers in chloroform. Similar results were reported by other authors (Hu, Chen, Xu, & Wang, 2011; Tingaut et al., 2010).

4.4. X-ray

The impact of chemical modification on the fiber crystal structure was evaluated using X-ray diffraction in order to determine how crystallinity was affected by the chemical modification performed in this study. The X-ray diffraction profiles of the cellulose before and after acetylation are given in Fig. 3. Unmodified cellulose display the typical XRD pattern of the native cellulose, with the main diffraction signals at around 2θ 14.9°, 16.2°, 22.5° and 34.3°. The acetylated cellulose also presented this diffraction pattern which indicates that the original structure of cellulose was maintained. Besides, the crystallinity index has remained constant around 0.7 after acetylation process which suggested that the modification has been limited to the surface of fibers or more accessible amorphous domains into the cellulose and did not affect crystalline regions in the cellulose. These results demonstrated that the fibers maintain reinforcement potential. Similar results were found by other authors for acetylated cellulose used to reinforce PLA (Tingaut et al., 2010; Tomé et al., 2011).

4.5. Films appearance

Bleached hemicellulose used to prepare composites was not able to form film without plasticizer. It was necessary to use 40% of plasticizer to form a film without cracks. However, acetylated hemicellulose was able to form film without the addition of any kind of

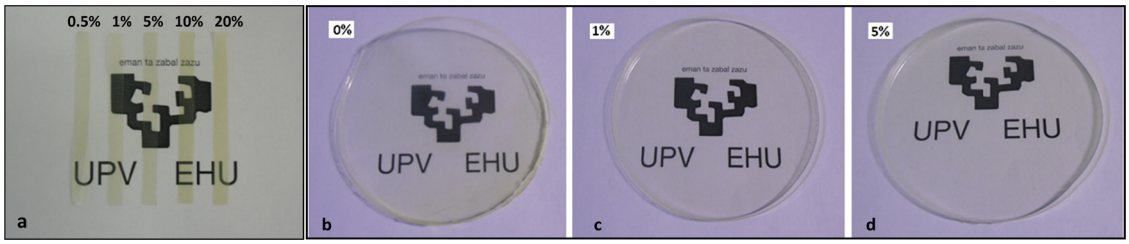

Fig. 4. Optical images of films: (a) test specimens of hydrophilic films with different percentages of nanofiber, (b) hydrophobic films without reinforcement, (c) hydrophobic films with 1% of acetylated cellulose and (d) hydrophobic films with 5% of acetylated cellulose.

additional substance. In both cases, the addition of cellulose (unmodified and acetylated) as reinforcement enhanced the formation of the film. All films were homogeneous without any visible particles presence as inspected by eyes. However, optical microscope showed the presence of some irregularly shaped agglomerates that could have been originated from less soluble fractions of used hemicellulose. Addition of cellulose did not cause a remarkable change in the films appearance. They did not lose their transparency with the addition of cellulose, but in the case of hydrophilic films showed a slight color change, being somewhat more yellowish at high percentages of cellulose in the composite. The hydrophobic films showed completely transparent appearance, no yellowish. The thickness of the films varied between 40 and 120 μm (Fig. 5).

4.6. Contact angle

The acetylation increases the hydrophobicity of the cellulose fibers and their adhesion to the hemicellulose acetylated matrix. The transformation of the surface characteristics of cellulose was further confirmed by the results of the contact angle measurements. As shown in Fig. 5, acetylated cellulose presented a sharp increase in θ_{water} from 48° to 73° due to the replacement of some of the surface hydroxyl groups with non-polar $-COCH_3$. A similar observation was reported by Lin et al. (2011).

Moreover, Fig. 6 proves that the hemicellulose acetylation considerably enhances the hydrophobic character of the obtained films. As can be observed, the film formed by bleached hemicellulose and glycerol (CBH) showed a contact angle around 57° while the film elaborated by acetylated hemicellulose (CBAH) was 72°. Also it demonstrated that increasing cellulose content in hydrophilic composites decreased the contact angle. This can be attributed to increased surface roughness and the introduction of a component more hydrophilic than the matrix. However, in composites formed by acetylated hemicellulose and acetylated cellulose the opposite happened, as it increases content of acetylated cellulose increases contact angle. Besides, during the time maintained hydrophobic behavior because very few degrees reduced the contact angle.

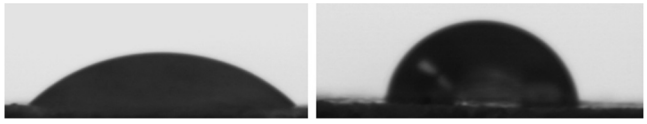

Fig. 5. Contact angle images: (left) unmodified cellulose, (right) acetylated cellulose.

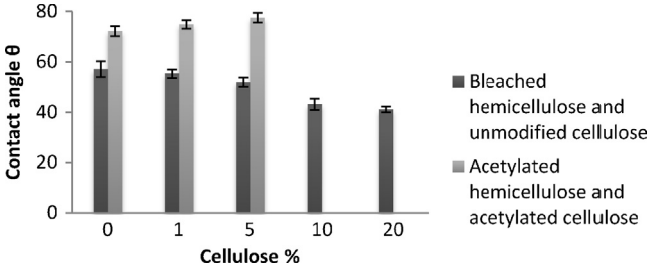

Fig. 6. Contact angle of composites.

4.7. Thermal analysis

The results of the thermal gravimetric analysis under nitrogen atmosphere of the different samples are shown in Fig. 7. The initial degradation temperature ($T_{5\%}$), the maximum weight loss temperature (T_{max}) and char residue al 600 °C have been analyzed. Fig. 7a showed thermal stability of the bleached and acetylated hemicelluloses. As can be seen, acetylated hemicellulose presented higher thermal stability than bleached hemicellulose. The initial degradation temperature corresponding to 5% weight loss ($T_{5\%}$) of acetylated hemicellulose (BAH) is marked higher than bleached hemicellulose (BH) with values of 334 °C and 239 °C respectively. The maximum weight loss rate in acetylated hemicellulose could be observed at 372 °C, while bleached hemicellulose showed a temperature of 303 °C. The solid residue at 600 °C for the bleached hemicellulose was 30% and 17% for acetylated hemicellulose. Similar behavior was found in other studies that modify hemicellulose (Fang et al., 2000; Grace et al., 2012; Jonoobi et al., 2012; Sun et al., 1999). This important improvement achieved after acetylation process, indicates higher thermal resistant behavior, desired for thermoplastic processing conditions. Furthermore, a change in thermal properties after chemical modification of cellulose was confirmed by TGA analysis. Fig. 7b showed that acetylated cellulose presented higher thermal stability than unmodified one. Similar results were obtained by other authors (Tingaut et al., 2010; Tomé et al., 2011; Urruzola, Serrano, Llano-Ponte, De Andrés, & Labidi, 2013). The initial degradation temperature ($T_{5\%}$) for unmodified cellulose was 212 °C, however, acetylated cellulose begins to degrade at higher temperatures $T_{5\%}$ = 305 °C. Besides, the maximum weight loss temperature (T_{max}) of original cellulose and acetylated was 350 °C and 366 °C, respectively. The solid residue at 600 °C for the unmodified cellulose and acetylated cellulose was 19% and 10%, respectively. In the case of the thermal stability of elaborated composites, bleached hemicellulose film with 40% glycerol (CBH) and composite with 10% of reinforcement (CBH10%) have been analyzed. In addition, acetylated hemicellulose film without reinforcement (CBAH) and with 5% acetylated reinforcement (CBAH5%) have also been analyzed. A significant improvement was obtained in the thermal behavior of the composites made from acetylated hemicellulose and acetylated cellulose respect to prepared with bleached hemicellulose and unmodified cellulose. Fig. 7c showed that the hydrophilic films had a small weight loss below 100 °C due to gradual evaporation of moisture followed by another small mass loss around 205 °C because of the presence of glycerol in both samples. As found in literature (Hansen et al., 2012), the content of glycerol in the films affects the thermal stability because it creates a plasticizing effect in the matrix increasing the free volume and generating less force between the two components

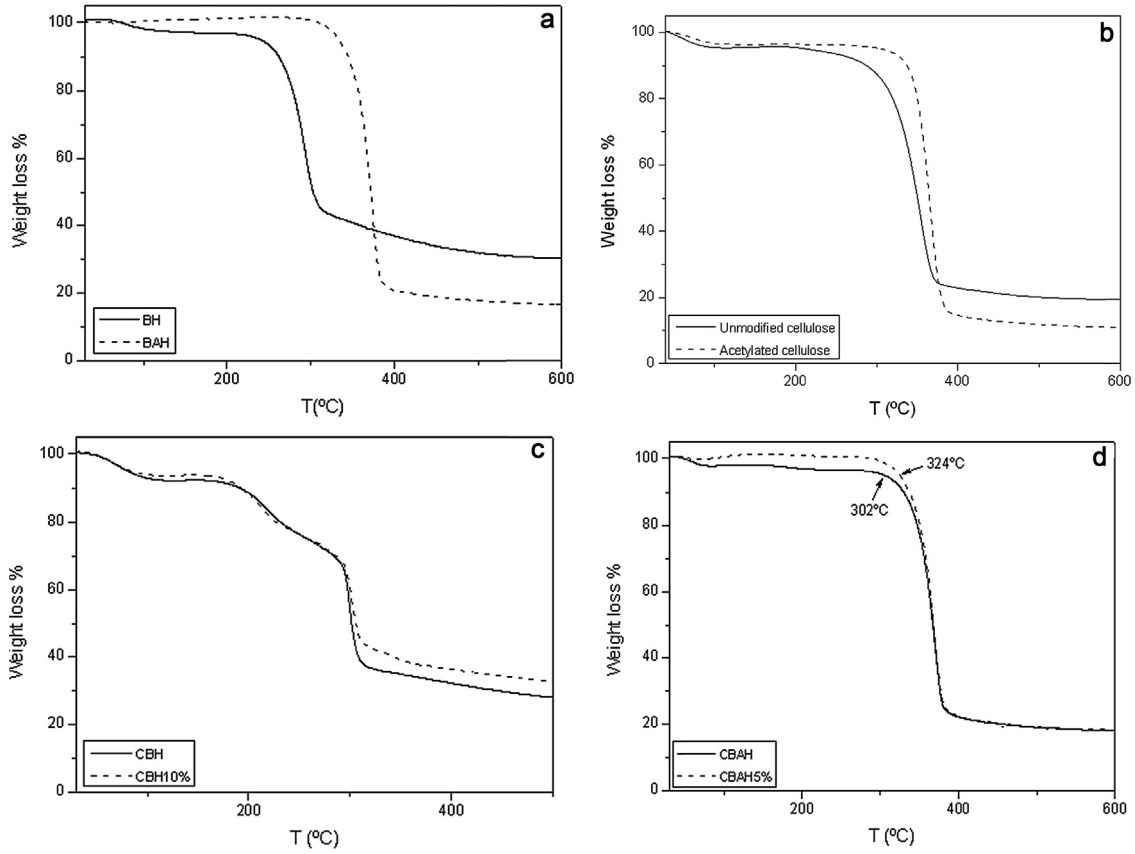

Fig. 7. Thermal stability of (a) bleached and acetylated hemicellulose, (b) unmodified and acetylated cellulose, (c) hydrophilic composites films without reinforcement (CBH) and with 10% of cellulose (CBH10%), and (d) hydrophobic composite films without reinforcement (CBAH) and with 5% of acetylated cellulose (CBAH5%).

of the material. The maximum weight loss rate was observed at 299 °C for composite without reinforcement and at 302 °C for film with 10% cellulose content. This demonstrates that the cellulose content increase thermal stability of the material in a few degrees as found in the literature. Composite containing 10% cellulose also presented another drop around 350 °C due to the presence of cellulose. Other type of composites, hydrophobic films, showed that although both films had the same maximum decomposition rate at 368 °C, composite film with 5% of acetylated cellulose begins to degrade later, at 324 °C, while unreinforced film start at 302 °C. The solid residue at 600 °C for the both composite films was the same around 18.5%.

4.8. Mechanical properties

The Young's modulus, tensile strain at break and tensile strength at break of the biocomposites are shown in Table 2. These tests were performed after specimens acclimate at 25 °C and 50% RH. The results demonstrate that the films obtained from bleached hemicellulose had poor properties but were improved with the addition of cellulose as reinforcement and plasticizer. Moreover the acetylation of bleached hemicellulose generated films with better mechanical properties, which were also improved by reinforcing with acetylated cellulose. In the case of hydrophilic films, up to 5% of cellulose as reinforcement had an increased strength and stiffness. The film without reinforcement and with 40% glycerol (CBH) showed a rather poor properties compared with those found in literature (Hansen et al., 2012; Peng et al., 2011). This film had little stiffness and strength but was quite ductile. However, the addition of 1% cellulose greatly enhanced all of the measured properties, exhibited greater stiffness and supported higher stress at break. The strain at break of this film seems to have improved, but it would be expected that the elongation will decrease with the reinforcement. Moreover, introducing 5% of cellulose continues to increase both the Young's modulus and strength, however, in this case the elongation decreases as expected. Although with 10% and 20% of cellulose as reinforcement properties were still better than the unreinforced matrix, these films showed a decrease in the properties compared to films with lower percentage of cellulose. The composite with 10% cellulose has greater stress at break than the others, presents a similar deformation to film with 5% cellulose, but decreases its stiffness. However, reinforcing 20% had a lower strength and stiffness but deformation remains around 12%. This decrease in properties at high percentages could probably be related to agglomerations due to poor dispersion of the reinforcement in the matrix and the use of high percentages. These agglomerations makes that exist a bad stress transfer between the reinforcement and the matrix and could generate weak structure by creating stress concentration points (Zhang, Zhang, Liang, & Lu, 2008). A similar thing happened to Stevanic et al. (2011) who reinforced arabinoxylan films with bacterial cellulose and found that the addition of 15% resulted in a decrease in the material strength by the presence of agglomerations. In general, it was found that the addition of a correct amount of reinforcement enhanced the performance of bleached hemicellulose films. On the other hand, hydrophobic films presented a much better mechanical properties than hydrophilic films. The experimental results indicate that the addition of acetylated cellulose improves the mechanical properties of the acetylated hemicellulose matrix. The improvement in mechanical properties has been by the use of an appropriate amount of reinforcement in the matrix, good dispersion of fibers and compatibility between the two components (Bulota, Kreitsmann, Hughes, & Paltakari, 2012). Film without reinforcement (CBAH) had similar properties that obtained by other authors (Mikkonen et al., 2012; Stepan et al.,

Table 2
Average values of tensile strength at break, strain at break and Young's modulus for composite films in tensile testing.

Cellulose content (%)	Hydrophilic films			Hydrophobic films		
	Bleached hemicellulose + cellulose			Acetylated hemicellulose + acetylated cellulose		
	Tensile strength (MPa)	Tensile strain (%)	Young's modulus (MPa)	Tensile strength (MPa)	Tensile strain (%)	Young's modulus (MPa)
0	3.3 ± 0.4	5.3 ± 1.7	3 ± 1	44.1 ± 2.9	5.7 ± 2.1	2300 ± 207
1	4.8 ± 0.4	19.7 ± 3.2	146 ± 29	48.5 ± 4.3	3.5 ± 1.0	2900 ± 228
5	5.8 ± 0.8	12.2 ± 4.9	206 ± 3	51.0 ± 1.9	2.9 ± 0.8	3200 ± 408
10	7.5 ± 1.2	12.4 ± 3.8	170 ± 12	–	–	–
20	4.5 ± 0.3	12.6 ± 1.4	90 ± 21	–	–	–

2012). The addition of acetylated cellulose as reinforcement in the matrix generated films that support higher stress at break. This happened because appropriate amounts of reinforcement were added into the material, thereby, prevented fibers auto-aggregation and favored the dispersion, thus generating stress concentration points in the matrix to contribute to the reinforcement (Lin et al., 2011). The stiffness was also increased with increasing content of acetylated cellulose. On the other hand, elongation at break decreased with the addition of reinforcement as expected. Similar behaviors have been found in literature when reinforced material with acetylated cellulose (Bulota et al., 2012; Jonoobi et al., 2012; Lin et al., 2011).

5. Conclusions

In this work, two types of composites were elaborated. Hemicellulose was extracted from corn cob. Ultrafiltration process was used with the aim to concentrate the liquor and retain high molecular weight components, which are more suitable for materials. Bleaching process was used as a purification method to remove the yellow color of original hemicellulose in order to be used as hydrophilic matrix. Commercial cellulose was used as reinforcement in hydrophilic films. Hemicellulose acetylation was performed to obtain a hydrophobic matrix and commercial cellulose was also acetylated to obtain better interactions between both components, which may be reflected in the improvement of the mechanical properties of the hydrophobic films. Acetylation of cellulose did not change its reinforcing potential. So the acetylation process was successful for obtaining films with greater hydrophobic character, high thermal stability and better mechanical properties than hydrophilic films.

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