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**Journal of Materials Science**

Full Set - Includes 'Journal of Materials Science Letters'

ISSN 0022-2461

Volume 48

Number 20

J Mater Sci (2013) 48:7196-7203

DOI 10.1007/s10853-013-7536-x



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# Bio-nanocomposites based on derivatized potato starch and cellulose, preparation and characterization

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Received: 28 January 2013 / Accepted: 13 June 2013 / Published online: 10 July 2013  
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**Abstract** The use of native starch as a thermoplastic polymer is limited by its fragility and high moisture absorption. Native potato starch was derivatized using different agents in order to reduce its hydrophobicity. A reduction in starch mechanical properties was also found as a side effect of derivatization treatments. The addition of nanocellulose allows to considerably improve mechanical properties of biopolymers as well as to maintain their inherent biodegradation capability. Cellulose nanofibers were added to native and modified starch in order to improve the mechanical properties. The mechanical properties of starch/cellulose nanocomposite films were evaluated, finding that they considerably improved with the addition of cellulosic nanofibers. This contribution demonstrates a new approach in order to produce bioplastics with combined effect: improved moisture and heat resistance (due to the chemical treatment) and high mechanical properties (after the addition of nanocellulose).

## Introduction

Natural biodegradable polymers appear as an attractive solution to the problems associated with the production,

use, and disposal of conventional plastics. Starch is a very attractive source for the development of biodegradable plastics. It is one of the lowest-cost biodegradable materials currently available in the global market [1, 2]. It can be found in the form of discrete semi-crystalline particles, whose size, shape, morphology, and composition depend on the botanical origin. These particles are called granules, and have a diameter ranging from 1 to 100  $\mu\text{m}$  and can present different regular or irregular shapes (spherical, oval, prismatic, and lenticular) [3–7]. Starch granules are partially crystalline and are composed mainly of two glucopyranose homopolymers: amylose and amylopectin. Starch granules are insoluble in water. The properties of starch depend largely on the amylose and amylopectin content as well as the shape and size of the granules. The presence of numerous hydroxyl groups determines the hydrophilic nature of starch.

While it is possible to produce plastics from native starch, they are not suitable for use as packaging material due to their poor mechanical properties and high moisture susceptibility [8]. As a result, numerous physical and chemical modification methods have been developed to enhance starch's positive characteristics, reduce its undesirable qualities, and add new attributes [9–16]. Other limitations associated with the use of native unmodified starch are its very high viscosity for low solid concentrations (which makes it difficult to process) and its high susceptibility to retrogradation (starch gels become opaque and bleed water). In previous contributions, the authors have demonstrated the utility of derivatizing potato starch, showing an important reduction in moisture sensitivity and an important increase in thermal stability [17].

In the last years, nanocomposite materials have gained much interest due to the remarkable improvement in properties. Incorporation of nanoparticles is an effective

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way of improving polymer performance. Investigation of their morphology and structure is essential to know the structure–property relationship of polymer composites [18].

Cellulose is the most abundant naturally occurring polymer on earth, and has become a very good source of nanoparticles for use as a reinforcing agent. The inherent stiffness and high degree of crystallinity make it ideally appropriate for reinforcing and load-bearing applications in composites. Other than this, cellulose is a sustainable resource, biodegradable in nature, inexpensive, and has low density. Cellulose is a polydisperse linear homopolymer consisting of  $\beta(1 \rightarrow 4)$  glycosidic linked D-glucose units, packed into elementary fibrils. This molecular structure and the uniform distribution of hydroxyl groups lead to the formation of several types of supra-molecular semicrystalline structures [19, 20]. The usual strategy adopted to isolate cellulose from the natural fibers consists in removing the matrix, which is made out of lignin and hemicellulose [21, 22]. Delignification is done by degrading the lignin molecules, dissolving them, and removing them by washing. Subsequently, the pulp can be bleached to obtain a product with lower amounts of impurities and improved aging resistance. Finally, controlled acid hydrolysis of the amorphous regions of native cellulose fibers disrupts the fibers which can then be dispersed into their constituent rod-shaped elementary crystalline microfibrils [17]. These cellulose nanofibrils can also be used to obtain composites [23].

Generally, the incorporation of nanofillers such as cellulose nanocrystals or clay platelets to thermoplastic starch produces a marked improvement in the mechanical properties. The characteristics of the interfacial bonding between the starch molecules and the filler nanoparticles

are critical to the nanocomposite material performance [24–27]. In this regard, the great chemical similarity and compatibility between starch and cellulose molecules promises a good reinforcing effect.

Several publications can be found in specific literature covering either the chemical modification of starch in order to reduce its hygroscopic nature [10, 12, 28] or the effect of the incorporation of nanofillers [24–27]. However, in this contribution we aim at producing a starch-based biocomposite with combined effect: improved moisture and heat resistance (due to the chemical treatment) and high mechanical properties (after the addition of nanocellulose).

## Materials and methods

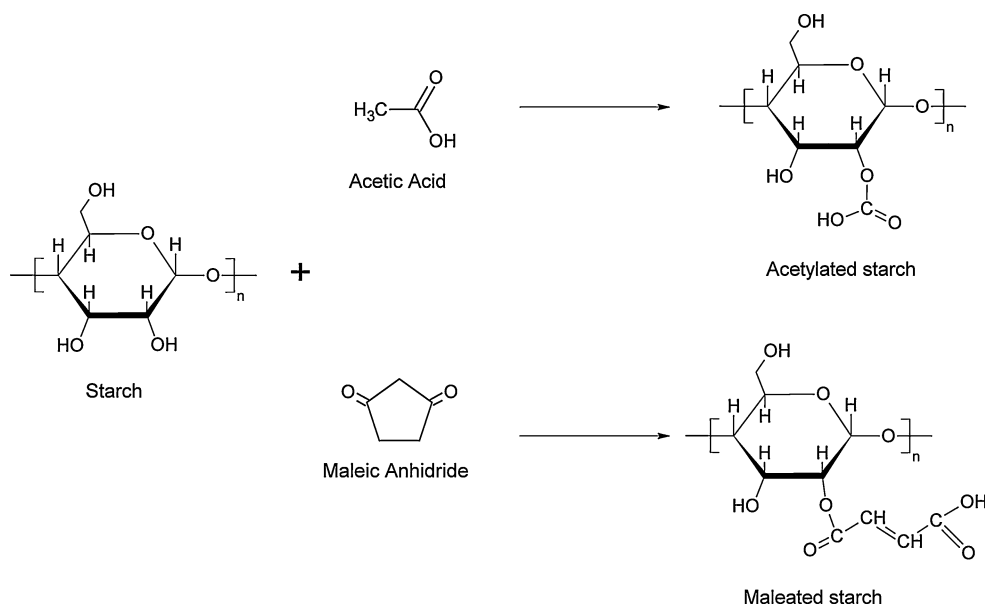
### Materials

Sisal fibers from Brascorda (Brazil) were used in this work. Native potato starch was kindly provided by Avebe Argentina SA (Argentina). Acetic acid and acetic anhydride were purchased from Cicarelli (Argentina). Glycerol, potato amylose, and amylopectin were purchased from Aldrich (USA). All other reagents used were of analytical grade.

### Chemical treatments for starch derivatization

Derivatization treatments were carried out using 0.1 mol of substituent per gram of starch according to previous works [17, 29]. Treatments were performed under the following conditions (Fig. 1):

**Fig. 1** Starch esterification reactions



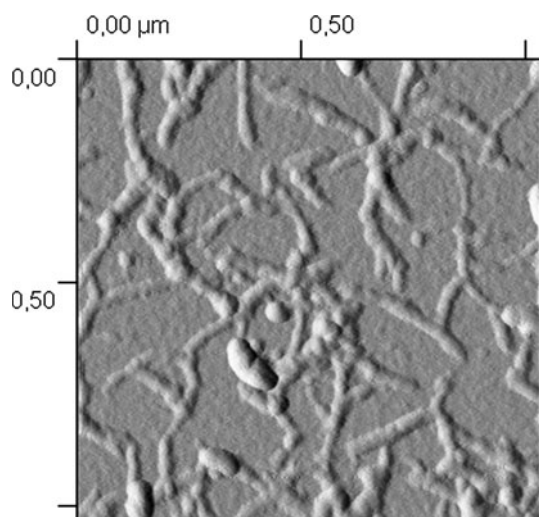
- Acetylation: 50 g of starch was immersed in a solution containing acetic acid (80 ml), acetic anhydride (40 ml), perchloric acid (0.5 ml), and toluene (100 ml) under constant stirring at room temperature for 4 h [29].
- Maleinization: 50 g of starch was immersed in a solution of maleic anhydride (5 g) in acetone (500 ml) under continuous stirring at room temperature for 24 h [29].

After derivatization, starch powder was recovered by filtration and dried at 40 °C for 48 h until constant weight was reached.

#### Preparation of cellulose nanofibers

Cellulose was extracted from sisal fibers (*Agave Sisalana*) using sodium chlorite, sodium bisulfite, and sodium hydroxide according to previous studies. Purified cellulose was subjected to acid hydrolysis ( $H_2SO_4$ ) in order to break amorphous sections, leading to cellulose nanofibers. Several methods were used in our previous contributions in order to characterize the obtained cellulosic nanofibers, such as TGA, DSC, FTIR, DRX, SEM, and atomic force microscopy (AFM). The acid hydrolysis was carried out with sulfuric acid ( $H_2SO_4$ ) solution 60 wt% at 45 °C, 30 min under continuous agitation. The overall procedure and nanofibers characterization can be found in previous contributions [30].

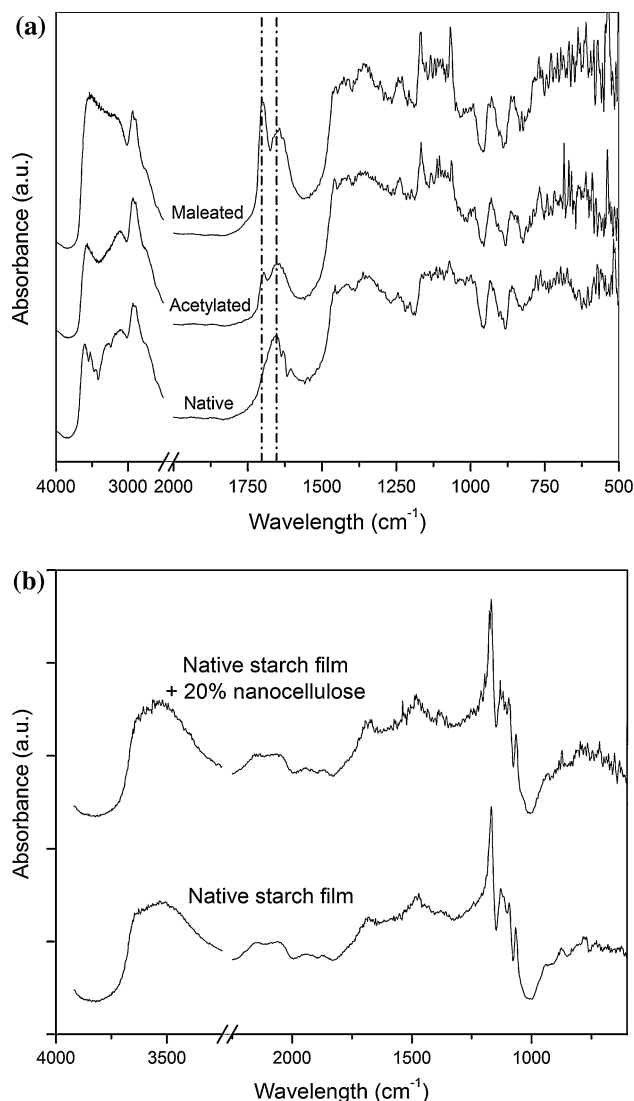
Figure 2 shows the AFM micrographs for the obtained nanocellulose [30]. A digital instruments NanoScope III controller with a multimode AFM head was used to image the cellulose crystals. Images were acquired in contact mode. The size of the nanocellulose fibers was measured by image analysis. The average diameter was  $30.9 \pm 12.5$  nm. These cellulose nanofibers were incorporated to native and treated starch.



**Fig. 2** Atomic force microscopy image of cellulosic nanofibers

#### Preparation of unreinforced and reinforced films from thermoplastic native and derivatized starch

In order to study the influence of the different derivatization treatments on the mechanical properties of potato starch, unreinforced films from native and modified starch were prepared by solvent evaporation method (casting). The general procedure followed for film preparation is described subsequently. Starch powder was dried in a vacuum oven at 40 °C for 48 h. In order to prepare thermoplastic starch films, starch granules must be completely gelatinized. Water is used as the main gelatinizing agent. Dry starch powder was mixed with appropriate amounts of plasticizer (glycerol) and excess water. The mixtures (starch 2 g, glycerol 0.6 g, and distilled water 50 ml) were heated to 75 °C under continuous stirring for 15 min. After complete gelatinization, 30 ml of



**Fig. 3** FTIR spectra for: **a** native and derivatized starch and **b** native starch with 20 % of nanocellulose

distilled water were added in order to chill the gel and reduce its viscosity to facilitate pouring into the molds. The gels were agitated by ultrasound for 5 min in order to remove air bubbles before placing in silicone molds. Afterward, the molds were placed in an oven at 35 °C for 48 h.

Nanocomposite films were prepared in a similar method. Fibers were added to the starch gel in an aqueous suspension during the gelatinization step under constant stirring. Native starch films containing 0, 2.5, 5, 10, and 20 wt% of nanocellulose were prepared. Afterward, modified starch films containing 5 wt% of nanocellulose fibers were obtained.

#### Fourier transformed infrared spectroscopy (FTIR)

The infrared spectroscopy technique has proved to be effective for evaluating the functional groups present in the chemical structure of various materials and has been used successfully in the study of different types of chemically modified starch [29, 31, 32].

A Mattson Genesis II FTIR was used to verify the effectiveness of the derivatization treatments. An average of 32 scans between 400 and 4000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  at room temperature was used. The obtained spectra were normalized considering the intensity of the peak at 2933  $\text{cm}^{-1}$ , which corresponds to the  $\text{CH}_2$  group. In the case of powder starch diffuse reflectance mode (DRIFT) was used. In the case of nanocomposite films attenuated total reflection (ATR) mode was used.

#### Contact angle determination

The influence of chemical modification on the surface polarity of starch films was studied by means of contact angle measurements. The method of the water drop was used to determine the contact angle [33]. Starch films were preconditioned for 48 h to 75 % RH. One drop of 5  $\mu\text{l}$  was placed on the surface of the films and an Olympus camera MV-50, 6 $\times$  zoom online with NIH Image Software was used. The contact angle was calculated from the shape of the drop according to the following equation:  $\theta = 2 \tan^{-1}(2h/d)$ . Three samples were tested for each material.

#### Mechanical properties

The mechanical properties of native and derivatized, reinforced and unreinforced starch films were determined according to ASTM-D638. The standard *bone-shaped* specimens were cut from solvent-cast films. A universal testing machine Instron 4467 was used. A high-precision optical extensometer was used for accurately determining the elastic modulus. Films were preconditioned at 75 % RH for 48 h prior to testing. Five samples were tested for each material.

## Results and discussion

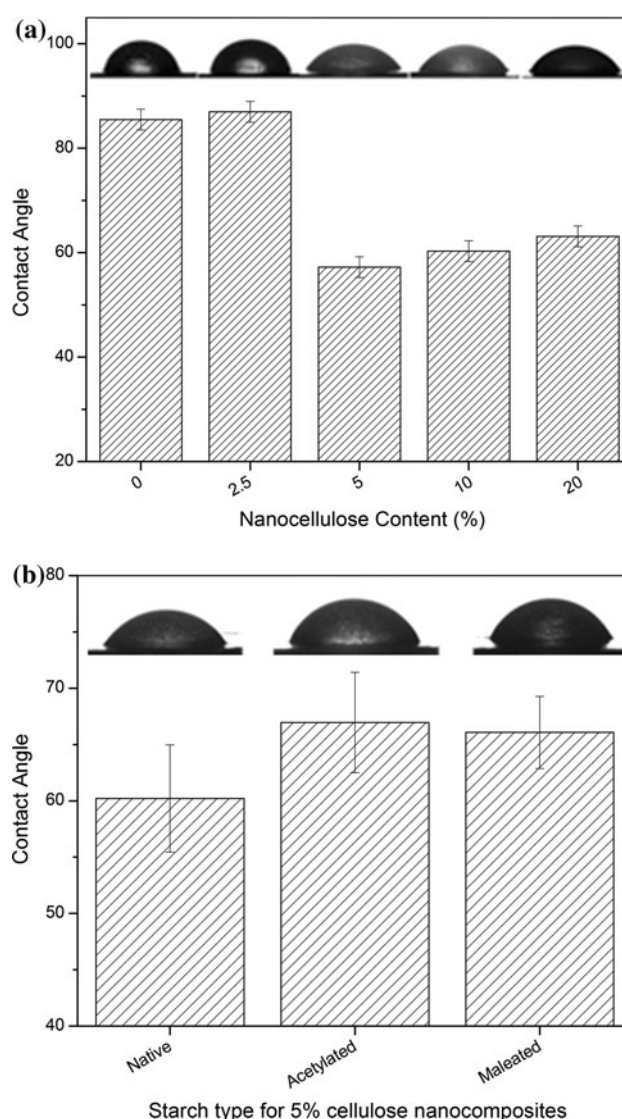
### Fourier transformed infrared spectroscopy

Native starch presents several characteristic absorbance bands and peaks (Fig. 3a). The region at 2880–2900 and 3200  $\text{cm}^{-1}$  corresponds to hydroxyl groups. The presence of  $\text{CH}_2$  groups determines the existence of the peaks at

**Table 1** Derivatization index based on IR spectra

Starch type	DI <sup>a</sup>
Acetylated	1.02
Maleated	0.33

<sup>a</sup> DI is an indicator of modification



**Fig. 4** Contact angle for **a** native starch reinforced with different amounts of nanocellulose and **b** derivatized starch containing 5% nanocellulose

**Table 2** Mechanical properties of native and derivatized potato starch films

Property	Native starch	Acetylated starch	Maleated starch
Elastic modulus (MPa)	234 ± 110	153 ± 63	169 ± 69
Strength (MPa)	7.5 ± 0.6	5.4 ± 1.1	6.6 ± 1.1
Elongation at break	0.34 ± 0.17	0.34 ± 0.06	0.45 ± 0.05

2920–2836, 2880, 1405–1465, and 1245  $\text{cm}^{-1}$ . The vibration of OH and CH groups in the glucopyranose rings is evidenced by the peaks at 1415 and 1320  $\text{cm}^{-1}$ . In addition, the peak at 1255  $\text{cm}^{-1}$  corresponds to the vibration of the CO group, while the peaks at 1150 and 1040  $\text{cm}^{-1}$  are related to the vibration of the COC group of the glycosidic bond.

Several differences were observed when analyzing the spectra of chemically modified starches. The spectra of modified starches show (Fig. 3a) a peak at 1703  $\text{cm}^{-1}$  corresponding to ( $\text{CO}_2$ ) groups and another peak at 1162  $\text{cm}^{-1}$ , which corresponds to the vibration of CO groups. An increase in the intensity of the peak at 1240  $\text{cm}^{-1}$  is also observed and is attributed to the presence of more CO groups. The presence of these peaks demonstrates the existence of ester groups and C=O bonds, which verifies the esterification of starch molecules [29]. In the case of acetylated starch, another peak appears at a wavelength of 1375  $\text{cm}^{-1}$  corresponding to the

deformation of C–CH<sub>3</sub> groups [32]. The incorporation of nanocellulose does not affect significantly the spectra of starch, due to the similar molecular structure of both polymers (Fig. 3b).

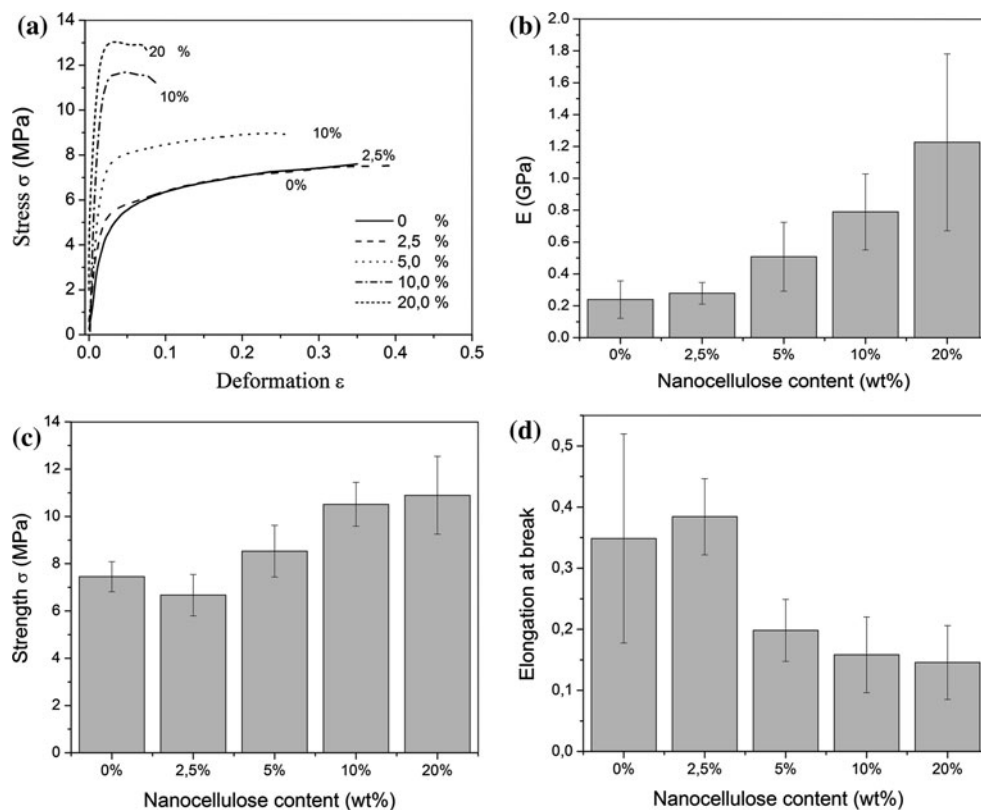
A derivatization index was calculated as the ratio of the intensity of the normalized ester peaks to the CH<sub>2</sub> peaks [34, 35]. This index is related to the amount of C=O esterification bonds created during the derivatization treatments and is an indicator of modification. Results are shown in Table 1.

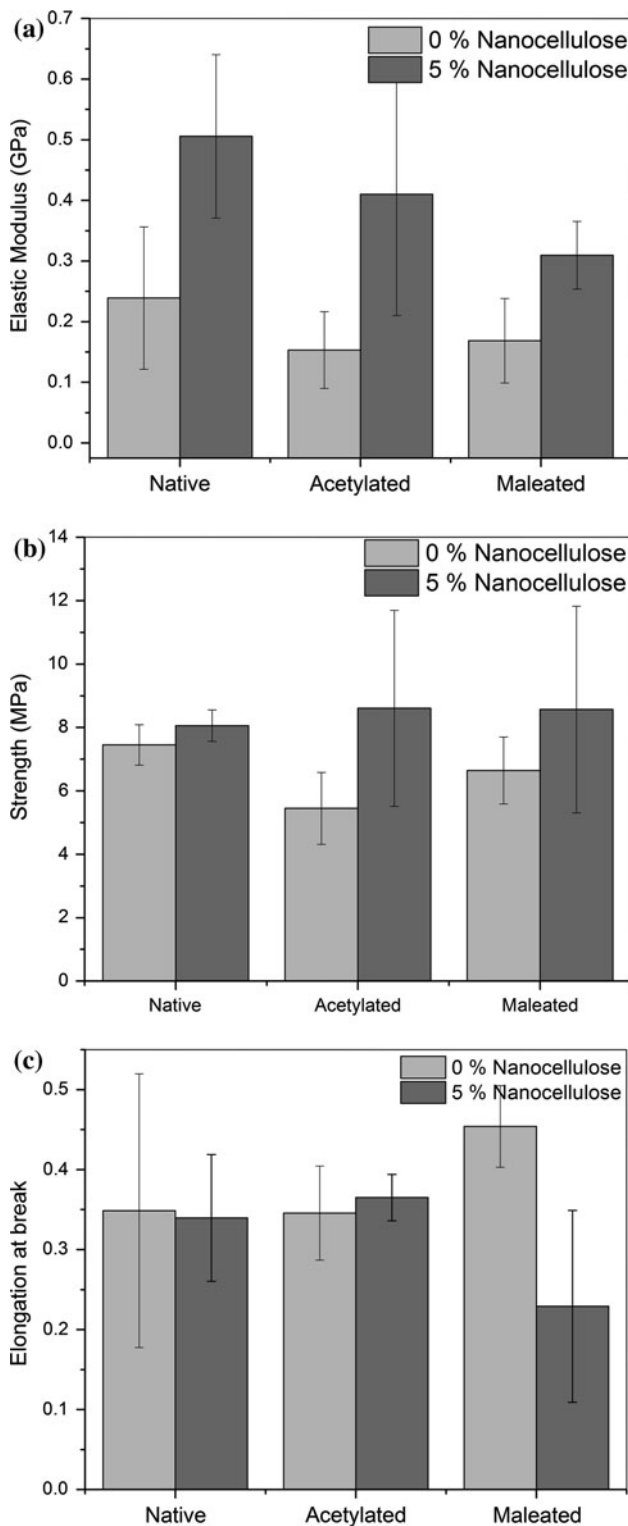
#### Contact angle determination

The determination of the contact angle permits to analyze the effects of the chemical treatments and the nanocellulose incorporation on the surface polarity of the films. The treatments produce an increase in contact angle and consequently a reduction in polarity, which involves an increment of the hydrophobic character of the surface [17]. This reduction presented by the modified starch films has been reported by several researchers [31, 36].

On the other hand, the incorporation of nanocellulose produces a diminution in the contact angle, thus an increase of polarity, due to the incorporation of more hydrophilic groups. The addition of only 2.5 % of nanocellulose does not produce any changes in the contact angle, but the incorporation of 5 % or more of nanocellulose produces as

**Fig. 5** Mechanical properties of native starch/nanocellulose composites: **a** Stress–strain curves for different cellulose contents, **b** young moduli calculated values for different cellulose contents, **c** strength for different cellulose contents, **d** elongation at break for different cellulose contents





**Fig. 6** Mechanical properties of native and derivatized starch-based nano-biocomposites: **a** elastic moduli for native and derivatized starch-based nano-biocomposites, **b** strength for native and derivatized starch-based nano-biocomposites, **c** elongation at break for native and derivatized starch-based nano-biocomposites

much as 30 % of decrease in the value of the contact angle, regardless of the amount of nanocellulose added (Fig. 4a).

The incorporation of nanocellulose to derivatized potato starch shows a similar effect than on native starch. However, due to the increased hydrophobicity of the resulting material, the contact angle is considerably higher than the one exhibited by the untreated potato starch (Fig. 4b).

#### Mechanical properties of native and derivatized starch films

The results of uniaxial tensile tests showed that the chemical modification of starch has a marked impact on the mechanical properties of films obtained from the different derivatized starches. Both, acetylated and maleated starch presented a reduced strength and elastic modulus. However, an increase in the elongation at break was observed for both materials (Table 2). The observed mechanical properties suggest a plasticizing effect caused by the introduction of bulky groups. This effect has been reported by other authors [32, 37–39].

#### Mechanical properties of nano-biocomposites

The nano-biocomposite films obtained from native starch were clear and homogeneous for the whole range examined (0–20 wt%).

The incorporation of cellulose nanofibers considerably improved starch mechanical properties as shown in Fig. 5a. This was attributed to the excellent compatibility among starch and cellulose molecules. Young modulus showed an important increase, which rises gradually together with the cellulose content (Fig. 5b). For low nanofiber contents, important improvements were observed. For 5 wt%, an increase higher than 100 % in the elastic modulus value was observed. Moreover, for 20 wt%, an increase of more than 500 % was observed. Accordingly, a gradual increase in strength was observed with the addition of cellulose nanofibers (Fig. 5c). Deformation at break values experienced the opposite effect, as it was expected (Fig. 5d). However, the samples remained ductile for the whole range of compositions studied. For low reinforcing contents, some plasticization effect was observed, mainly attributed to the scale of the reinforcing phase. This effect persists for all fiber contents analyzed, but is hindered by the reinforcing effect. The high reinforcing effect has been attributed to the great chemical compatibility between starch and cellulose molecules [40–43].

The reinforcement effect of cellulose nanofibers was studied for contents ranging from 0 to 20 wt%. However,



due to the high cost associated with the extraction and preparation of cellulose nanofibers, only the usage of small amounts of it is viable. Formerly, it was demonstrated that really high reinforcement effects (Young modulus increase of up to 100 %) can be obtained by using as low as 5 wt% of nanofibers in native potato starch films.

Therefore, nano-biocomposites based on derivatized potato starch were prepared using only 5 wt% of cellulose nanofibers. Similarly, a marked reinforcement effect was observed (Fig. 6a–c). The elastic modulus increased more than 100 % in all cases. When related to the native starch unreinforced films, the resulting reinforcement effect appeared to be lower but still very interesting. For instance, the 5 % reinforced acetylated starch film presented an elastic modulus 167 % higher than its unreinforced counterpart and 70 % higher than the unmodified, unreinforced starch film (Fig. 6a).

## Conclusions

The properties of nanocomposites with celluloses obtained by casting from water dispersion of nanocellulose and gelatinized and plastisized starch have been investigated. In this contribution, both the disadvantages of starch (moisture sensitivity and low mechanical properties) were simultaneously reduced, by chemical derivatization on one side and reinforcement with highly compatible nano-sized cellulose fibers on the other. It was shown that chemical modification treatments have a plasticizing effect on starch films, changing their mechanical properties. A reduction in elastic modulus and resistance together with no modification or a slight increase in elongation at break was observed.

In this contribution, it was shown that the incorporation of cellulose nanofibers conducted to an important improvement in starch films mechanical properties, even for fiber contents as low as 5 wt%. Finally, derivatized starch was reinforced by adding 5 wt% of cellulose nanofibers, not only recovering its mechanical properties but also improving by more than 100 % the elastic modulus and 10 % the strength when compared to native starch.

This paper demonstrates an interesting approach to obtain completely biodegradable starch, cellulose-based bioplastics with reduced hydrophilicity and improved mechanical properties.

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