Carbohydrate Polymers 93 (2013) 307–315

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of cellulose reinforcement on the properties of organic acid modified starch microparticles/plasticized starch bio-composite films

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A R T I C L E   I N F O

Article history:
Received 29 October 2011
Received in revised form 8 August 2012
Accepted 8 October 2012
Available online 26 October 2012

Keywords:
Starch
Cellulose
Bio-composite
Thermal properties
Mechanical testing
Water resistance

A B S T R A C T

The present paper describes the preparation and characterization of polysaccharides-based bio-composite films obtained by the incorporation of 10, 20 and 30 wt% birch cellulose (BC) within a glycerol plasticized matrix constituted by the corn starch (S) and chemical modified starch microparticles (MS). The obtained materials (coded as MS/S, respectively MS/S/BC) were further characterized. FTIR spectroscopy and X-ray diffraction were used to evidence structural and crystallinity changes in starch based films. Morphological, thermal, mechanical, and water resistance properties were also investigated. Addition of cellulose alongside modified starch microparticles determined a slightly improvement of the starch-based films water resistance. Some reduction of water uptake for any given time was observed mainly for samples containing 30% BC. Some compatibility occurred between MS and BC fillers, as evidenced by mechanical properties. Tensile strength increased from 5.9 to 15.1 MPa when BC content varied from 0 to 30%, while elongation at break decreased significantly.

1. Introduction

New materials obtained from renewable resources have gained much attention in the last decades due to the global increasing demand for alternatives to fossil resources (Belgacem & Gandini, 2008). At the same time, the use of natural polymers as reinforcing elements in composite materials presents important advantages when compared with their synthetic or inorganic counterparts. Composites based on polymers filled with natural fibers, also called eco-composites (Bogoeva et al., 2007) have attracted the even growing attention from both scientific and industrial point of view (Avella et al., 1997; Awal, Ghosh, & Sain, 2010; Bouza et al., 2008; Joshi, Drzal, Mohanty, & Arora, 2004). Among several classes of polymeric matrices, polyolefins are the most used to realize natural fiber reinforced composites (Ichazo, Alberno, Gonzalez, Perera, & Candal, 2001; Woodhams, Thomas, & Rogers, 1984; Zhang, Endo, Qiu, Yang, & Hirotsu, 2002). Unless virgin cellulose fibers are mainly used as reinforcement in composites, in the last years recycled cellulose has been also proposed, in many cases with very promising results, with the aim of contributing to the serious waste management problem (Baroulaki et al., 2006; Huda, Mohanty, Drzal, Schut, & Misra, 2005). Valorization of carbohydrates, oils, lignin, and other materials from lignocellulosics provides a promising opportunity and a processing facility for development of sustainable integrated bio-refinery processes for bio-based materials production.

Starch and cellulose are two biopolymers with the potential advantages such as low cost, available from renewable resources and enabling to replace some synthetic polymers (Choi, Kim, & Park, 1999; Martins et al., 2009; Mohanty, Misra, & Hinrichsen, 2000). However, their inherent disadvantages (high water absorbency of starch, the poor solubility of cellulose, and low tensile property), have limited their wider applications (Samir, Alloin, & Dufresne, 2005). Main sources of starch are represented by corn (the largest one), as well as by potato, rice, pea and others (Albertsson & Karlsson, 1995). It can be used in its granular form or as biodegradable filler (Wang, Yang, & Wang, 2003). It becomes thermoplastic when properly plasticized with water or other plasticizers – glycerol, sorbitol, and other low-molecular weight polyhydroxy compounds (Carvalho, Job, Alves, Curvelo, & Gandini, 2003; Gaudin, Lourdin, Forssell, & Colonna, 2000). To improve its properties, starch is usually blended with other thermoplastic polymers (Chen, Cao, Chang, & Huneault, 2008; Cordoba, Cuellar, Gonzalez, & Medina, 2008; Ma, Yu, & Kennedy, 2005; Ma, Yu, & Wang, 2007; Wang, Yu, Ma, & Wu, 2007; Wang, Yu, Chang, & Ma, 2008). The mechanical properties of starch polymer matrix could be significantly improved in the presence of natural fillers as reinforcements (Cao, Chen, Chang, Muir, & Falk, 2008; Müller, Laurindo, & Yamashita, 2009; Savadekar & Mhaske, 2012).

Starch is often chemically modified by partial or complete esterification of the hydroxyl groups in the side chain (Tomasik & Schilling, 2004). The introduction of an ester group provides

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http://dx.doi.org/10.1016/j.carbpol.2012.10.020

hydrophobic character, and changes thermal and mechanical properties of starch-derived products. Starch-based composite films reinforced with chemically modified starch have a stable structure under ambient conditions, good resistance to water uptake, and better mechanical properties than those without modified starch. Citric acid modified starch, for example, represents a granular resistant starch which improved the tensile strength and water vapor barrier properties when it was used as reinforcing agent within glycerol-plasticized thermoplastic starch matrix (Ma, Chang, Yu, & Stumborg, 2009). Tartaric acid, like other hydroxy acids (citric, lactic), is commonly met in several natural products and play a significant role in food preparation and preservation.

Cellulose is a natural polymer, with a very long molecular chain, consisting of only one repeating unit, glucose, and occurring in crystalline state (Hagenmaier & Shaw, 1990). Several studies (Amash & Zugenmaier, 2000; Bledzki & Gassan, 1999; Dufresne & Vignon, 1998; Funke, Bergthaller, & Lindhauer, 1998; Wollerdorfer & Bader, 1998) and applications have demonstrated the use of cellulose as reinforcement in thermoplastic matrices. According to Dufresne and Vignon (1998), the water resistance of starch-based plastics can be improved by adding a small amount of commercial cellulose fibers up to 15% (w/w). Adding other polysaccharide materials could improve not only the corn starch film water resistance but also the mechanical functionality (Chandra & Rustgi, 1998).

In the present work, the modified corn starch microparticles were obtained by reaction with tartaric acid (Ma, Jian, Chang, & Yu, 2008; Ma, Chang, & Yu, 2008) and further incorporated within a glycerol plasticized corn starch matrix in order to obtain starch-based films used as control. Bleached birch cellulose pulp was used as reinforcement at different loading levels within corn starch based films and its influence upon mechanical and physical properties was investigated. All the components (starch, cellulose, glycerol) have a hydrophilic nature allowing them to adhere well in films due to hydrogen bonding. By addition of modified corn starch microparticles within the plasticized starch matrix it can be envisaged the improvement of water resistance for different packaging applications. Nevertheless, this can be achieved probably due to remaining cross-linking activity within the previously prepared modified starch microparticles. Polysaccharide-based composites were characterized through different methods such as X-ray diffraction, FTIR spectroscopy, scanning electron microscopy (SEM), thermal analysis, and water absorption tests. Mechanical properties as tensile strength and elongation at break were also evaluated.

2. Materials and methods

2.1. Materials

Natural cellulose (bleached birch pulp obtained from *Betula verrucosa*) was provided by Sodra Company (Sweden). Its chemical composition is as follows: 74.8% cellulose, 23.6% xylan, 1.1% glucomannan, and 0.4% lignin. The characteristics of birch cellulose sample are as follows: coarseness-to-width ratio 6.17 g/m^2, fiber length 1.1-1.5 mm, and fiber width 6-22 μm, respectively. Cellulose sample was previously fine grounded in a Retsch PM 200 planetary ball mill for a better dispersion in composite films. The cellulose particle size was determined using laser diffraction (Mastersizer 2000, Malvern Instruments), when resulted a wide size distribution with less uniformity and high volume fractions of larger particles (from 200 μm to 1450 μm). The mean particle size of cellulose powder has following values: $d(0.1) = 230.221\ \mu$m, $d(0.5) = 533.755\ \mu$m and $d(0.9) = 1017.174\ \mu$m. Corn starch (S), glycerol, tartaric acid (TA) and ethanol (all analytical grade) were supplied by Chemical Co. Iasi (Romania), being used as received.

2.2. Preparation of tartaric acid modified starch microparticles

Corn starch (S; 10 g) was added into 200 ml of distilled water. The mixture was heated at 90 °C for 1 h for the complete gelatinization of corn starch with constant stirring, and then 200 ml of ethanol was added dropwise to the solution of gelatinized starch solution with constant stirring. When the resulting starch microparticles suspensions were cooled at the room temperature, another 200 ml of ethanol was added dropwise for about 50 min with constant stirring. The suspensions were centrifuged at 8000 rpm for 20 min, and the settled starch microparticles were washed using ethanol to remove the water. After complete washing, the starch microparticles were dried at 50 °C to remove ethanol.

Tartaric acid (20 g) was dissolved in 100 ml of ethanol. Starch microparticles (3.5 g) was mixed with 15 ml of tartaric acid solution in a glass tray and conditioned for 12 h at room temperature to allow the absorption of tartaric acid solution by starch microparticles. The tray was dried in vacuum oven at about 2 mmHg and 50 °C for 6 h to remove ethanol. The obtained mixture was ground and dried in a forced air oven for 1.5 h at 130 °C. The dry mixture was washed three times with water to remove non-reacted tartaric acid. Tartaric acid-modified starch microparticles (MS) were finally washed with ethanol to remove water, dried at room temperature, and ground. The dried MS was used for obtainment of composite films with different percent of birch cellulose. The molar degree of substitution (DS) was determined (Ma, Jian, et al., 2008; Ma, Chang, et al., 2008) in triplicate, the mean value being 0.067 ± 0.005.

2.3. Obtainment of polysaccharide-based bio-composite films

The chemically modified starch (MS) was dispersed in a solution of distilled water (100 ml) and glycerol (1.5 g) for 1 h before adding 5 g corn starch and birch cellulose (BC). MS filler loading level (4 wt%), as well as the birch cellulose loading level (10%, 20% and 30% respectively) was based on the amount of starch. The higher the MS content within the glycerol plasticized starch matrix is, the greater the tensile strength of the starch-based composite, due to the intrinsic adhesion of the filler-matrix interface caused by the chemical similarity (polysaccharide structure) of starch and modified starch. However, the higher MS filler content may induce the conglomeration, which reduces the effectiveness of filler (Ma et al., 2009).

The mixture was heated at 90 °C for 0.5 h with constant stirring. To obtain the MS/S/BC bio-composite film, the mixture was cast using a fast coating technique namely the doctor blade technique. Bio-composite samples were obtained by dropping and spreading the mixture on a glass plate using a blade with a slit width of 0.8 mm. After degassing in a vacuum oven at 50 °C for 24 h up to constant weight, the bio-composite films were air cooled and detached from the glass surface to be investigated. Films with a thickness of ~0.2 mm were obtained, this value resulting from measurements by means of a digital micrometer. The samples, coded as MS/S/BC10, MS/S/BC20, respectively MS/S/BC30, were further characterized by different techniques and preconditioned in a climate chamber at 25 °C and 50% RH for at least 48 h prior to the mechanical testing.

2.4. X-ray diffraction

The crystalline structure of the bio-composites was studied by XRD using a Bruker AD8 ADVANCE X-ray diffractometer with Cu Kα radiation at 60 kV and 50 mA, at room temperature. Scattered radiation was detected in the diffraction angle 2θ ranging from 10 to 30° at a rate of 2° min^{-1}.

2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of bio-composite samples were recorded on a Bruker Vertex 70 spectrophotometer. The spectral resolution was 4 cm^{-1} and the scanning range varied from 400 to 4000 cm^{-1}.

2.6. Scanning electron microscopy (SEM)

For the SEM investigation, samples with surface areas of about 5 mm × 5 mm were cut from the different oven-dried bio-composite products. The cross-sections were smoothed by several successive microtome cuttings. The samples were mounted on special stubs using carbon tabs and were then coated with gold by sputtering under vacuum (10^{-2} mbar). The surface properties of specimens were investigated using a scanning electron microscope (QUANTA 200).

2.7. Thermal analysis

TG/DTG/DSC analysis was performed using a Netzsch STA 449 F1 Jupiter system under nitrogen atmosphere. The measurements were performed while heating the samples (~5 mg) placed in Al_2O_3 crucibles hermetically closed with lids at a rate of 10 °C/min from room temperature up to 600 °C and using nitrogen as a purging gas at a flow rate of 50 ml/min. TG curves recorded with a ±0.5 °C precision were analyzed using a Netzsch Proteus analysis software.

2.8. Mechanical properties

Tensile stress and strain at break were evaluated according to ASTM D882-00 (ASTM D882-00 Standard Test Method for Tensile Properties of Thin Plastic Sheeting) using an Instron 3345 with a 5-kN load cell. Before testing, the films were cut into strips and conditioned at 50% RH and 25 °C for 48 h. Testing was done on samples each measuring 10 cm × 1 cm randomly cut from the cast films. The thickness of each specimen was measured at four points along its length with digital micrometer. The crosshead speed was 10 mm/min. A minimum of 10 replications of each test sample were run.

2.9. Water uptake

To determine the water absorption (Dufresne & Vignon, 1998), the bio-composite specimens used were thin rectangular strips with dimensions of 10 mm × 10 mm × 0.2 mm. The samples were supposed to be thin enough so that the molecular diffusion was considered to be one-dimensional and were vacuum-dried at 90 °C overnight. After weighing, samples were conditioned at 25 °C in a desiccator containing sodium sulfate in order to ensure a relative humidity (RH) of 95%. The conditioning of samples in high moisture atmosphere was preferred to the classical technique of immersion in water, because starch is very sensitive to water and can partially dissolve after long time exposure to water. The samples were removed at specific intervals and gently blotted with tissue paper to remove the excess of water on the surface, and the water uptake was calculated with Eq. (1), as follows:

$$\text{water uptake } (\%) = \frac{W_t - W_0}{W_0} \times 100 \tag{1}$$

where W_t and W_0 represents the bio-composite sample weight at time t and before exposure to 95% RH, respectively. The determinations were performed in triplicate.

3. Results and discussion

3.1. X-ray diffraction

The semi-crystalline characters of corn starch (S), modified corn starch (MS), birch cellulose (BC), and modified starch/starch/birch cellulose bio-composite samples (MS/S/BC) are revealed from the diffractograms illustrated in Fig. 1a–c. Native corn starch is known to have a distinct crystalline form namely the A-type. The typical A-type structure present in native starch leads to diffraction peaks at 15.3°, 17.5° and 23.1°. These diffraction peaks have disappeared in MS. The BC presents diffraction peaks at 15.7° and 22.1°, these being assigned to the typical reflection planes of cellulose I.

In modified starch, introducing tartaric acid groups has an effect on A-type starch (normal corn starch). When TA penetrates the starch granule through channels and cavities, it could disrupt the crystalline structure of granules, thus the V_H-type crystallinity occurs in MS during thermal processing, with major reflections at $2\theta = 13.2°$, and 19.2°. The peaks at $2\theta = 15.3°$ (corn starch), respectively at $2\theta = 13.2°$ (MS), disappeared in MS/S/BC composite samples, indicating that the long-range ordered structure of normal corn starch was almost completely disrupted during composites processing.

When starch is gelatinized, the A-type structure was destroyed. In the case of the modified starch/starch samples (Fig. 1b), new sharp peaks appear at 17.2°, 19.9° and 22.2°. Similar peak positions have been reported for gelatinized plasticized corn starch (Kim, Na, & Park, 2003; Myllärinen, Buleon, Lahtinen, & Forssell, 2002). With addition of bleached birch cellulose at different loading level values, the starch-based films present high intense diffraction peaks with no significant differences between them as evidenced in Fig. 1b. However, if cellulose is present, new structures may form through blending with corn starch and plasticizer (glycerol). This is reflected in the shape and intensity of the diffraction peaks when the cellulose is added and starch/cellulose ratio is varied. The bio-composite samples filled with 10, 20 and 30 wt% birch cellulose (Fig. 1b) show the same crystalline structures as the unfilled bio-composites, but the intensity of the diffraction peak specific to cellulose ($2\theta = 22.2°$) increases as cellulose content increases.

3.2. FTIR spectroscopy

The FTIR spectra of S, MS, BC and MS/S/BC bio-composite samples are shown in Fig. 2. Infrared spectra of corn starch exhibited complex vibration modes at low wave-number values (below 800 cm^{-1}) due to the skeletal mode vibrations of the glucose pyranose ring (Santha, Sudha, Vijaykumari, Nayar, & Moorthy, 1990; Sekkal, Dincq, Legrand, & Huvenne, 1995). The region between 800 and 1500 cm^{-1} provided highly overlapping and complex spectra making the exact band assignment difficult (Tu, Lee, & Milanovich, 1979).

A new peak occurred at 1742 cm^{-1} is assigned to C=O stretching vibration in MS (Fig. 2). The presence of the carbonyl peak indicates that starch microparticles were successfully reacted with tartaric acid. In S the oxygen of the C—O—C group could form the hydrogen-bond interaction with the hydrogen of hydroxyl groups, while the ester bonds in MS as the cross-linking of starch sterically hindered this hydrogen-bond interaction. The weakening of this interaction made C—O bond stretching of the C—O—C group shifted to 1020 cm^{-1}. The band at 1078 cm^{-1} is due to CH—O—CH_2 stretching (Biswal & Singh, 2004).

The band absorption at 3425 cm^{-1}, specific to amorphous cellulose (Hinterstoisser & Salmén, 1999; Kondo & Sawatari, 1996), is attributed to the O—H stretching being related to the intra-molecular hydrogen bonds at the C-3 position, but also possible intra-molecular hydrogen bonds between the functional groups at

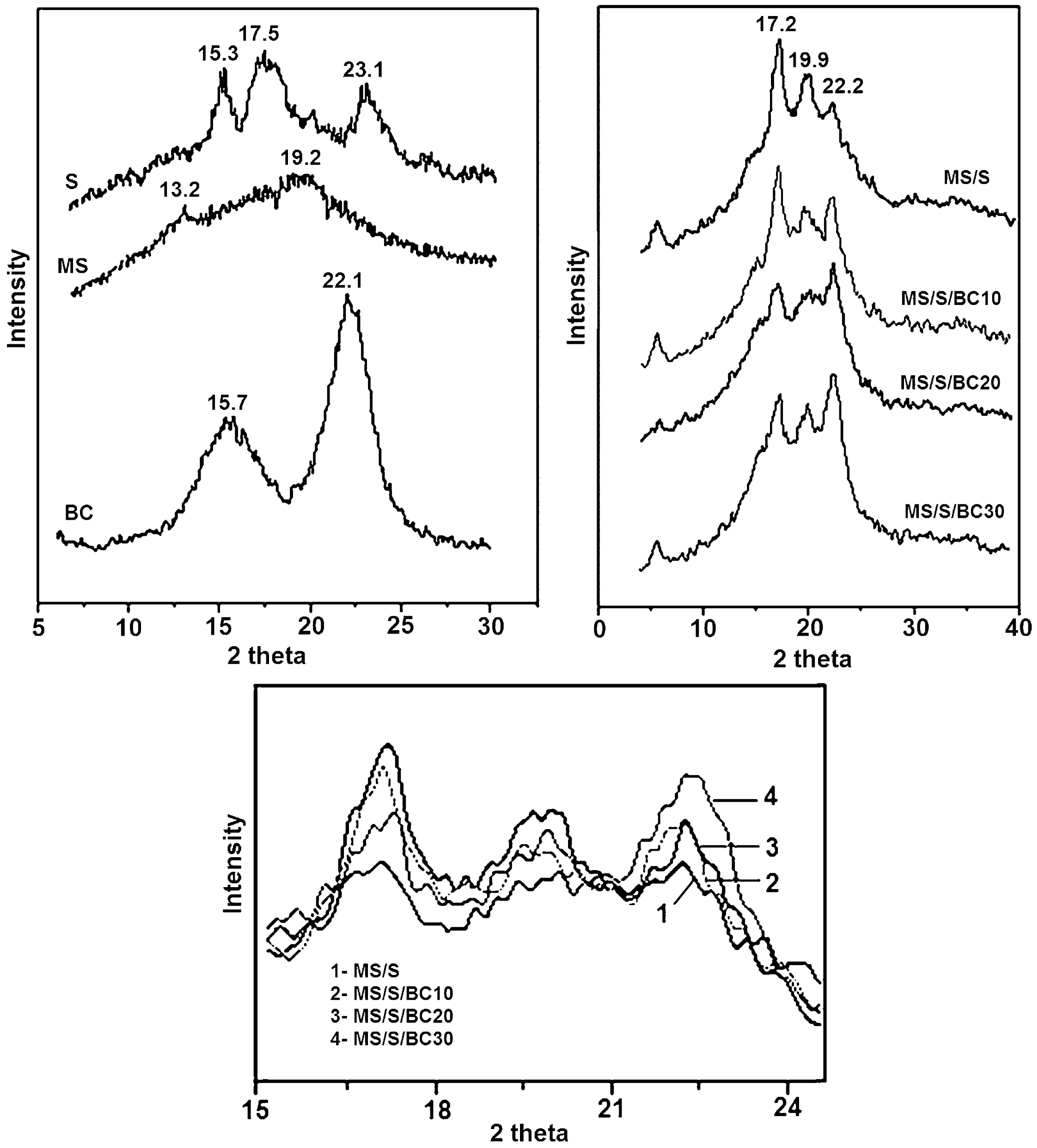

Fig. 1. X-ray diffraction curves for starch–cellulose bio-composite films.

the C-2 and C-6 positions in cellulose. Technical celluloses, such as bleached wood pulp, contain additional carbonyl and carboxyl groups as a result of the isolation and purification processes that play a significantly role in the processing of cellulose (Klemm, Heublein, Fink, & Bohn, 2005; Rőhrling, Potthast, Rosenau, Sixta, & Kosma, 2002).

Some modifications in the FT-IR spectra of composites (spectra not represented here) indicate that the anti-symmetric and symmetric vibrations of C=O and C—O bonds were enhanced, probably due to the disruption of intermolecular H-bonds between carboxylic groups caused by blending modified corn starch and BC.

All the changes in wave number indicate obvious interactions among the hydroxyl and carbonyl groups of the starch and cellulose components (Kondo & Sawatari, 1996; Pandey, 1999). These changes can be attributed to the hydrogen bonding possibly occurred between hydroxyl, carbonyl groups in both starch and cellulose.

3.3. *Scanning electron microscopy (SEM)*

The SEM micrographs for polysaccharide-based bio-composite samples are presented in Fig. 3a–h.

The modified corn starch film presents a relative smooth morphology. Compared with modified corn starch film, the surface morphology of the existence of the BC in the corn starch matrix can be easily observed in the composite films. However, it is difficult to distinguish the individual BC filler dispersion due to its small size. Some BC fillers appear as white domains at the surface of the sample. The selection of SEM micrographs of the fractured surface of bio-composite samples is shown in Fig. 3e–h. For each sample, two different magnifications were used in order to display both the cellulose dispersion within the starch matrix and the interfacial adhesion between the two polysaccharide components. As it can be observed, this fact is due to their good dispersion of within the plasticized starch matrix, without noticeable aggregates due their breakage. Obviously, in the case of BC, only the small mat fragments were observed. These results clearly corroborated the superior mechanical properties of the modified starch-BC bio-composite samples compared with those without BC, as suggested by the mechanical tests discussed below. It was difficult to identify the cellulose fibers from the plasticized starch matrix; this is usually the case when there is good adhesion between the matrix and fibers because the fibers are coated with the polymer. Nevertheless, the mechanical interlocking is better in this system because of the

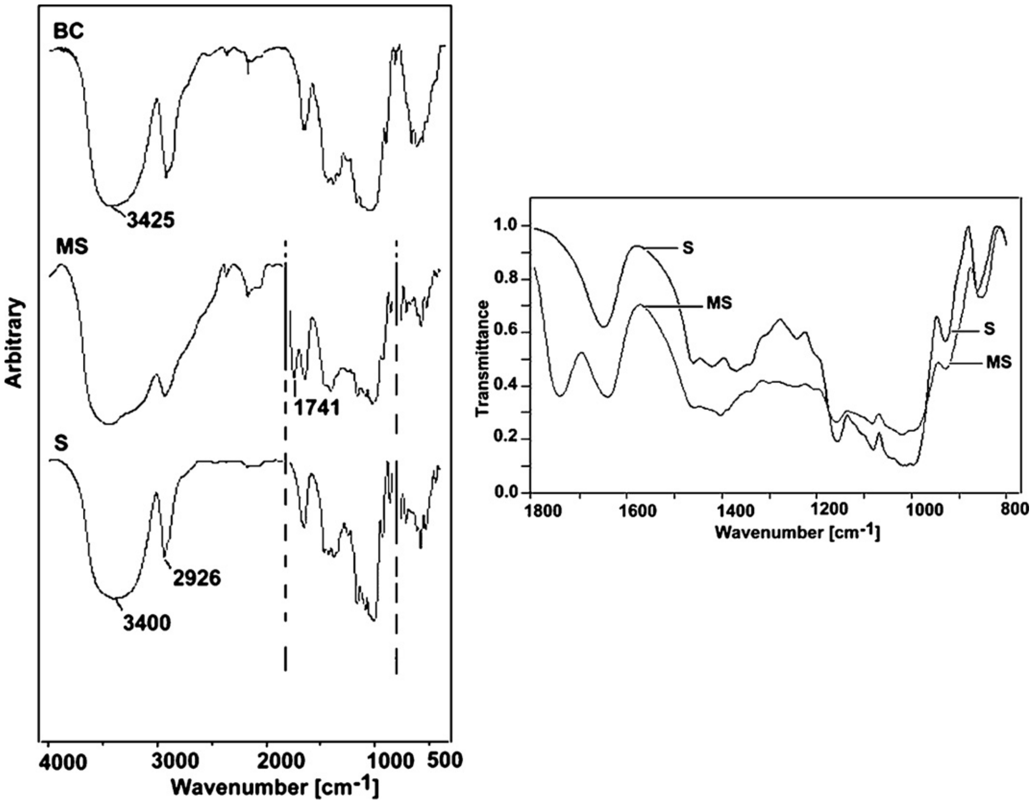

Fig. 2. FTIR spectra of S, MS and BC.

roughness of the wood flour and that might contribute to improved adhesion.

3.4. Mechanical properties of the composite films

The tensile strength and elongation at break of the modified corn starch (MS) and reinforced with birch cellulose bio-composite films is represented in Fig. 4. This figure clearly demonstrates the reinforcing effect of BC fillers. The tensile strength of the bio-composite films increased when increasing the BC fillers content from 0 to 30% (Fig. 4a) and this indicated that some compatibility occurs between starch matrix and BC fillers and the performances (e.g., mechanical properties). Cellulose has a ribbon-like and hence more linear three-dimensional structure than starch and offers the possibility of more extensive and indeed cooperative behavior of the hydrogen bonds. Thus, cellulose addition induces variation of properties, due to the formation of a three-dimensional network between the different carbohydrates through hydrogen bonds (Dufresne & Vignon, 1998; Dufresne, Dupeyre, & Vignon, 2000).

At 50% RH, modified corn starch based films containing BC had significantly higher tensile strength but lower elongation at break than control. This means that addition of cellulose generates strong interactions between cellulose fibers and between cellulose and starch matrix which restricts the chain motion of starch matrix (Bledzki & Gassan, 1999).

These results were consistent with literature data corn starch-based bio-composites (Ghanbarzadeh, Almasi, & Entezami, 2010) and pea starch composites films (Ma, Jian, et al., 2008; Ma, Chang, et al., 2008)

3.5. TG–DTG–DSC analysis

Three characteristic thermal transitions may exist for semi-crystalline polymers such as starch: a glass transition for the amorphous fraction, a melting transition for the crystalline fraction and a transition due to crystallization. The DSC thermograms of the starch, MS/S and MS/S/BC bio-composite samples exhibited sharp endothermic peaks (typical of a semi-crystalline polymeric system) – see Fig. 5. These endothermic peaks have been associated with the melting of crystalline starch and BC domains re-organization. The main thermal parameters are shown in Table 1.

Table 1
Thermal parameters for modified starch/plasticized starch, respectively modified starch/plasticized starch/cellulose bio-composite films.

Sample	DSC data			DTG data	
	Endothermic peak (°C)			T_{peak} (°C)	Mass change (%)
MS/S	138.1	297.1	318.5	321.5	89.48
MS/S/BC10	131.2	292.8	322.1	322.3	89.23
MS/S/BC20	122.8	290.4	322.6	320.9	89.08
MS/S/BC30	112.5	280.0	322.5	322.5	89.81

A small weight loss of about 2–5% below 100 °C is assigned to the release of moisture from the samples. All of the composite samples show one-stage degradation within the range of 230–420 °C (Fig. 5). The residual weight of the composite films beyond 500 °C slightly increases for MS/S/BC30 composite film. The maximum decomposition temperatures of the composite films (T_{max} = 320–330 °C) are higher than that of modified starch/plasticized starch (T_{max} = 310 °C), showing relatively high thermal stability because of the enhancement of inter-molecular hydrogen bonds among biopolymers in the blend films.

It should be noted that a strong shoulder in DTG curves appeared at 350 °C for all MS/S/BC film samples, which can be assigned to the starch and cellulose decomposition processes. All film samples under thermal study exhibit another shoulder at around 287 °C which can be related to the presence of some hemicelluloses in BC, as well as to the different amounts of non-absorbed glycerol by modified starch and cellulose.

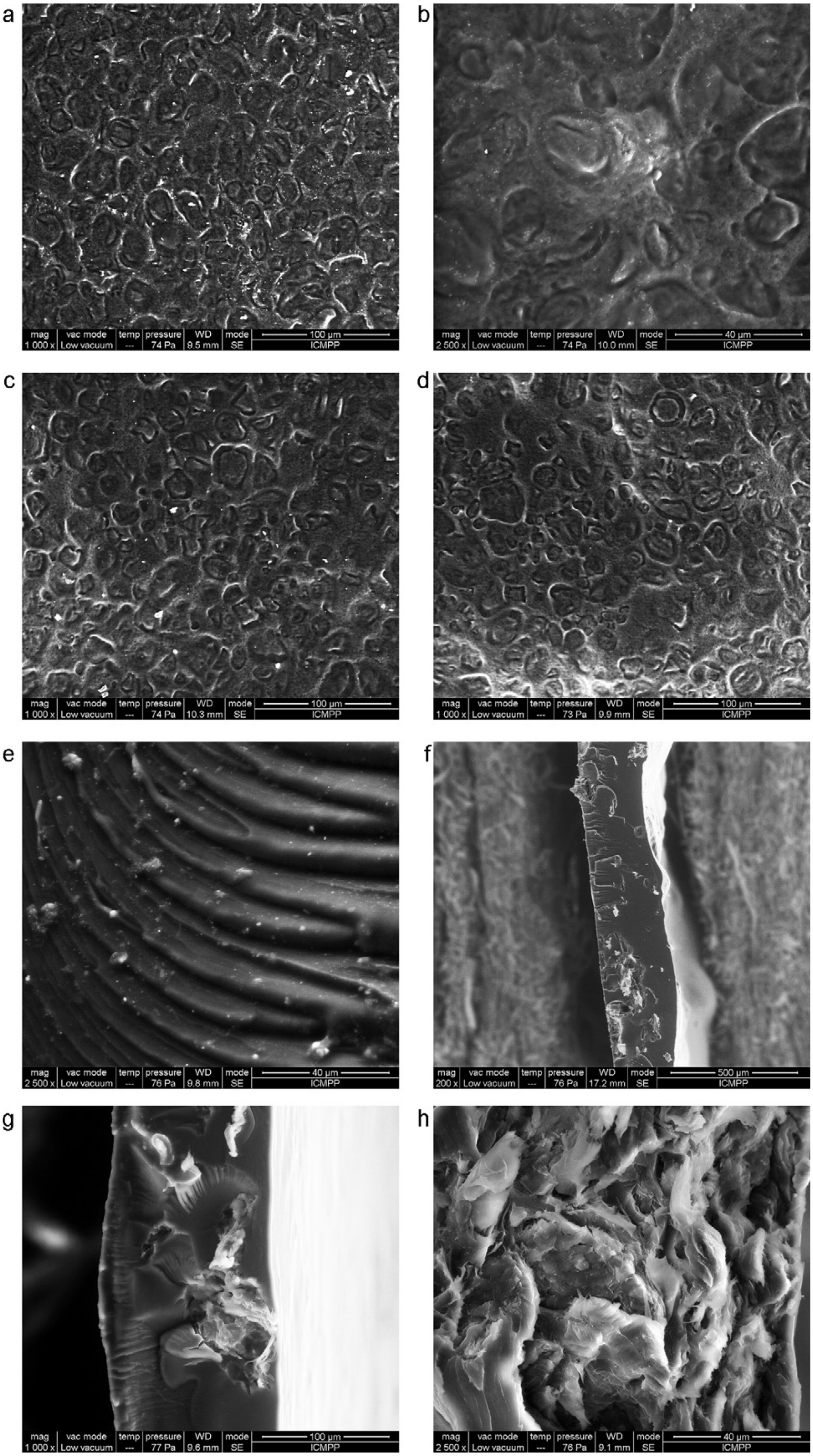

Fig. 3. SEM micrographs of corn starch/plasticized starch and starch/cellulose bio-composite samples: (a) MS/S; (b) MS/S/BC10; (c) MS/S/BC20; (d) MS/S/BC30, respectively the fragile fractured surface of samples (e) MS/S; (f) MS/S/BC10; (g) MS/S/BC20; (h) MS/S/BC30.

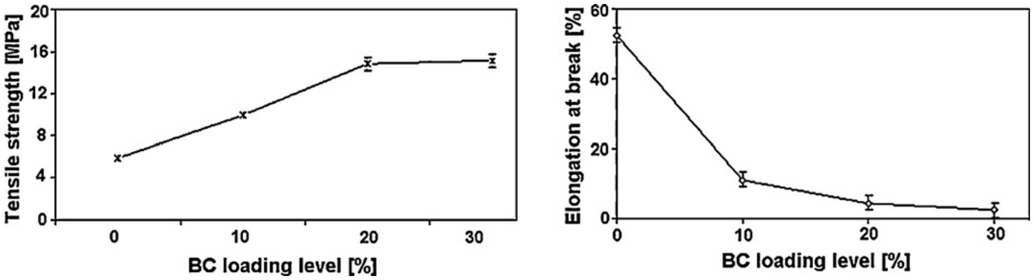

Fig. 4. Effect of BC loading level on the mechanical properties of the polysaccharide-based bio-composite films: (a) tensile strength and (b) elongation at break at 50% RH and 25 °C.

The melting peak of MS/S was around 138.1 °C, higher than that for starch–cellulose bio-composites. For MS/S/BC samples, the temperature position of the melting peak decreased from 138.1 °C to 112.5 °C and 297.1 °C to 280.0 °C, respectively as BC content increased from 0 to 30% (w/w). The change in the position of this peak indicates that higher BC contents favor the formation of larger crystal domains and lowers the mobility of the amylopectin (Mondragon, Arroyo, & Romero-Garcia, 2008).

3.6. Water uptake

In a multiple biopolymer system, each biopolymer not only contributes to the film properties alone but also engages in biopolymer–biopolymer interactions that affect the overall system properties. Occasionally, these interactions are more important than individual actions (Ban, Song, Argyropoulos, & Lucia, 2006; Ban, Song, & Lucia, 2007).

Because starch films are very sensitive to changes in moisture that results in changes in their mechanical properties, controlling the film moisture content is highly important. Hence, the water resistance provided by cellulose fibers is significant for new applications that are moisture sensitive such as gas selective membranes, and ion channels.

Water uptake of modified starch/cellulose bio-composite films depended on the BC loading level (Fig. 6).

Addition of organic acid modified starch within a glycerol plasticized starch matrix can induce a slightly improvement of the film water resistance mainly during first 5 h of water absorption test comparatively with film no containing modified starch (Spiridon, Teaca, & Bodirlau, 2011). As it is shown in Fig. 6, incorporation of various amounts of cellulose within the starch based polymer matrix containing modified starch microparticles reduces to a less extent the water uptake of these films. Some differences are observed by addition and increasing cellulose amount within film samples during water absorption tests. By comparison, we can observe a reduction of water uptake with increasing cellulose amount up to 30% for all time values. Thus, considering MS/S and MS/S/BC30 film samples, reduction of water absorption follows the order: 11.44% (after 5 h) > 9.34% (after 75 h) > 9.29% (after 100 h). The kinetics of water absorption exhibited two-well

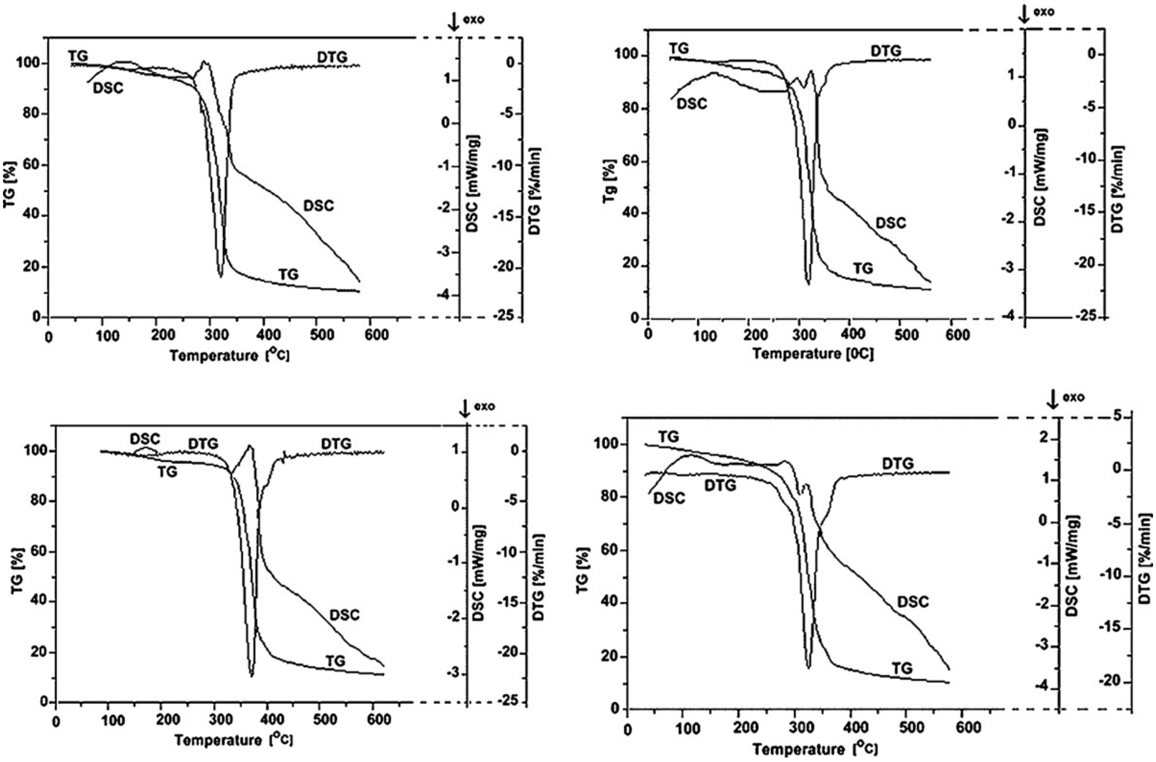

Fig. 5. TG–DTG–DSC curves for polysaccharide-based bio-composite films: (a) MS/S; (b) MS/S/BC10; (c) MS/S/BC20; (d) MS/S/BC30.

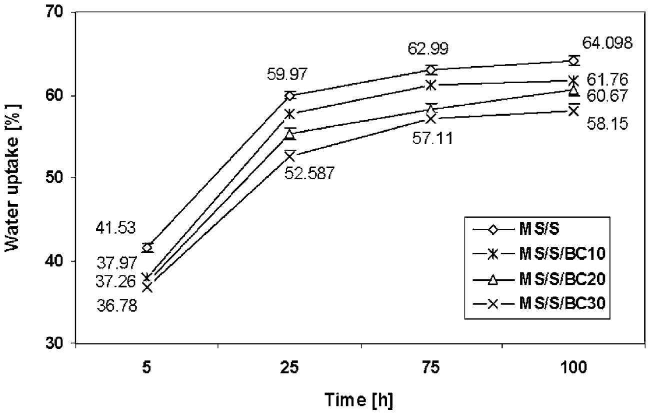

Fig. 6. Effect of BC loading level on the water uptake of polysaccharide-based bio-composite films at 25 °C.

separated zones, the first one being fast ($t < 75$ h), the second one being relatively slow (it reaches a plateau). The water uptake for a given time is always as low as the cellulose amount is high.

The decreased water uptake indicated that intermolecular interaction occurred between starch and BC in the polysaccharide-based bio-composite samples. The hydroxyl group of BC can form strong hydrogen bonds with the hydroxyl groups on starch, thus improving the interactions between molecules, improving the cohesiveness of the biopolymer matrix, and decreasing the water uptake (Dufresne & Vignon, 1998; Ma, Jian, et al., 2008; Ma, Chang, et al., 2008; Müller et al., 2009). Nevertheless, the results of water sorption experiments can be also explained by the presence of some hemicelluloses (xylan) in cellulose sample which are more hydrophobe than cellulose.

4. Conclusions

Polysaccharide-based bio-composite films have been obtained by introduction of birch cellulose (BC) at different loading levels within a glycerol plasticized corn starch matrix containing previously synthesized tartaric acid modified starch microparticles.

X-ray diffraction and FTIR spectroscopy evidenced the changes in the crystallinity and structure of the corn starch and modified starch based composite films. Introducing organic acid groups in corn starch granules affected their crystalline structure. Some diffraction peaks at $2\theta = 15.3^\circ$ (corn starch), respectively at $2\theta = 13.2^\circ$ (MS), disappeared in MS/S/BC composite samples, indicating that the long-range ordered structure of normal corn starch was almost completely disrupted during composites processing. FTIR spectra evidenced interactions between films constituent polysaccharides, starch and cellulose.

A good dispersion of the MS and BC within the plasticized starch matrix was evidenced by SEM analysis. Addition of BC alongside MS determined a slightly improvement of the starch-based films water resistance. At 50% RH, MS/S/BC films presented significantly higher tensile strength but lower elongation at break than control, fact which gives evidence of strong interactions between cellulose fibers and between cellulose and starch by restricting the chain motion of starch matrix.

Thermal analysis indicated an improvement to some degree of starch based films stability by incorporating cellulose as evidenced by the maximum decomposition temperature values. Such polysaccharide-based films have an environmentally friendly nature and can be useful for different packaging applications.

Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007–2013 under grant agreement no CP-IP 228589-2 AFORE, respectively the project no. 119EU/29.03.2011.

References

Albertsson, A. C., & Karlsson, S. (1995). Degradable polymers for the future. *Acta Polymerica*, *46*, 114–123.

Amash, A., & Zugenmaier, P. (2000). Morphology and properties of isotropic and oriented samples of cellulose fibre–polypropylene composites. *Polymer*, *41*(4), 1589–1596.

Avella, M., Casale, L., Dell'Erba, R., Focher, B., Martuscelli, E., & Marzetti, A. (1997). Broom fibers as reinforcing materials for polypropylene-based composites. *Journal of Applied Polymer Science*, *68*(7), 1077–1089.

Awal, A., Ghosh, S. B., & Sain, M. (2010). Thermal properties and spectral characterization of wood pulp reinforced bio-composite fibers. *Journal of Thermal Analysis and Calorimetry*, *99*(2), 695–701.

Ban, W., Song, J., Argyropoulos, D. S., & Lucia, L. A. (2006). Improving the physical and chemical functionality of starch-derived films with biopolymers. *Journal of Applied Polymer Science*, *100*, 2542–2548.

Ban, W., Song, J., & Lucia, L. A. (2007). Influence of natural biomaterials on the absorbency and transparency of starch-derived films: An optimization study. *Industrial Engineering & Chemistry Research*, *46*, 6480–6485.

Baroulaki, I., Mergos, J. A., Pappa, G., Tarantili, P. A., Economides, D., Magoulas, K., et al. (2006). Performance of polyolefin composites containing recycled paper fibers. *Polymers for Advanced Technologies*, *17*(11–12), 954–966.

Belgacem, M. N., & Gandini, A. (2008). *Monomers, polymers and composites from renewable resources*. Amsterdam: Elsevier.

Biswal, D. R., & Singh, R. P. (2004). Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers*, *57*, 379–387.

Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, *24*(2), 221–274.

Bogoeva, G., Avella, M., Malinconico, M., Buzarovska, A., Grozdanov, A., Gentile, G., et al. (2007). Natural fiber eco-composites. *Polymer Composites*, *28*(1), 98–107.

Bouza, R., Marco, C., Ellis, G., Martin, Z., Gomez, M. A., & Barral, L. (2008). Analysis of the isothermal crystallization of polypropylene/wood flour composites. *Journal of Thermal Analysis and Calorimetry*, *94*(1), 119–127.

Cao, X., Chen, Y., Chang, P. R., Muir, A. D., & Falk, G. (2008). Starch-based nanocomposites reinforced with flax cellulose nanocrystals. *Express Polymer Letters*, *2*, 502–510.

Carvalho, A. J. F., Job, A. E., Alves, N., Curvelo, A. A. S., & Gandini, A. (2003). Thermoplastic starch/natural rubber blends. *Carbohydrate Polymers*, *53*, 95–99.

Chandra, R., & Rustgi, R. (1998). Biodegradable polymers. *Progress in Polymer Science*, *23*, 1273–1335.

Chen, Y., Cao, X., Chang, P. R., & Huneault, M. A. (2008). Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. *Carbohydrate Polymers*, *73*, 8–17.

Choi, E. J., Kim, C. H., & Park, J. K. (1999). Structure–property relationship in PCL/starch blend compatibilized with starch-g-PCL copolymer. *Journal of Polymer Science Part B: Polymer Physics*, *37*, 2430–2438.

Cordoba, A., Cuellar, N., Gonzalez, M., & Medina, J. (2008). The plasticizing effect of alginate on the thermoplastic starch/glycerin blends. *Carbohydrate Polymers*, *73*, 409–416.

Dufresne, A., Dupeyre, D., & Vignon, M. R. (2000). Cellulose microfibrils from potato tuber cells: Processing and characterization of starch–cellulose microfibril composites. *Journal of Applied Polymer Science*, *76*(14), 2080–2092.

Dufresne, A., & Vignon, M. R. (1998). Improvement of starch film performances using cellulose microfibrils. *Macromolecules*, *31*(8), 2693–2696.

Funke, U., Bergthaller, W., & Lindhauer, M. G. (1998). Processing and characterization of biodegradable products based on starch. *Polymer Degradation and Stability*, *59*(1–3), 293–296.

Gaudin, S., Lourdin, D., Forssell, P. M., & Colonna, P. (2000). Antiplasticisation and oxygen permeability of starch-sorbitol films. *Carbohydrate Polymers*, *43*, 33–37.

Ghanbarzadeh, B., Almasi, H., & Entezami, A. A. (2010). Physical properties of edible modified starch/carboxymethyl cellulose films. *Innovative Food Science & Emerging Technologies*, *11*, 697–702.

Hagenmaier, R. D., & Shaw, P. E. (1990). Moisture permeability of edible films made with fatty acid and hydroxypropylmethylcellulose. *Journal of Agriculture and Food Chemistry*, *38*, 1799–1803.

Hinterstoisser, B., & Salmén, L. (1999). Two-dimensional step-scan FTIR: A tool to unravel the OH valency-range of the spectrum of Cellulose I. *Cellulose*, *6*, 251–263.

Huda, M. S., Mohanty, A. K., Drzal, L. T., Schut, E., & Misra, M. (2005). Composite materials "Green" composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation. *Journal of Materials Science*, *40*, 4221–4229.

Ichazo, M. N., Alberno, A., Gonzalez, J., Perera, R., & Candal, M. V. (2001). Polypropylene/wood flour composites: Treatments and properties. *Composite Structures*, *54*, 207–214.

Joshi, S. V., Drzal, L. T., Mohanty, A. K., & Arora, S. (2004). Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Journal of Composites A*, *35*, 371–376.

Kim, D. H., Na, S. K., & Park, J. S. (2003). Preparation and characterization of modified starch-based plastic film reinforced with short pulp fiber. I. Structural properties. *Journal of Applied Polymer Science*, *88*, 2100–2107.

Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, *44*, 3358–3393.

Kondo, T., & Sawatari, C. (1996). A Fourier transform infra-red spectroscopic analysis of the character of hydrogen bonds in amorphous cellulose. *Polymer*, *37*, 393–399.

Ma, X., Chang, P. R., & Yu, J. (2008). Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrate Polymers*, *72*, 369–375.

Ma, X., Chang, P. R., Yu, J., & Stumborg, M. (2009). Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites. *Carbohydrate Polymers*, *75*, 1–8.

Ma, X., Jian, R., Chang, P. R., & Yu, J. (2008). Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. *Biomacromolecules*, *9*(11), 3314–3320.

Ma, X., Yu, J., & Kennedy, J. F. (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate Polymers*, *62*, 19–24.

Ma, X. F., Yu, J. G., & Wang, N. (2007). Fly ash-reinforced thermoplastic starch composites. *Carbohydrate Polymers*, *67*, 32–39.

Martins, M. G. I., Magina, S. P., Oliveira, L., Freire, C. S. R., Silvestre, A. J. D., Neto, C. P., et al. (2009). New biocomposites based on thermoplastic starch and bacterial cellulose. *Composites Science and Technology*, *69*(13), 2163–2168.

Mohanty, A. K., Misra, M., & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites. An overview. *Macromolecular Materials and Engineering*, *276/277*, 1–24.

Mondragon, M., Arroyo, K., & Romero-Garcia, J. (2008). Biocomposites of thermoplastic starch with surfactant. *Carbohydrate Polymers*, *74*, 201–208.

Müller, C. M. O., Laurindo, J. B., & Yamashita, F. (2009). Effect of cellulose fibers on the crystallinity and mechanical properties of starch-based films at different relative humidity values. *Carbohydrate Polymers*, *77*, 293–299.

Myllärinen, P., Buleon, A., Lahtinen, R., & Forssell, P. (2002). The crystallinity of amylose and amylopectin films. *Carbohydrate Polymers*, *48*, 41–48.

Pandey, K. K. (1999). A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. *Journal of Applied Polymer Science*, *71*, 1969–1975.

Rőhrling, J., Potthast, A., Rosenau, T., Sixta, H., & Kosma, P. (2002). Determination of carbonyl functions in cellulosic substrates. *Lenzinger Berichte*, *81*, 89–97.

Samir, M. A. S. A., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, *6*, 612–626.

Santha, N., Sudha, K. G., Vijaykumari, K. P., Nayar, V. U., & Moorthy, S. N. (1990). Raman and infrared spectra of starch samples of sweet potato and cassava. *Proceedings of the Indian Academy of Science (Chemical Sciences)*, *102*, 705–712.

Savadekar, N. R., & Mhaske, S. T. (2012). Synthesis of nano cellulose fibers and effect on thermoplastics starch based films. *Carbohydrate Polymers*, *89*(1), 146–151.

Sekkal, M., Dincq, V., Legrand, P., & Huvenne, J. P. (1995). Investigation of the glycosidic linkages in several oligosaccharides using FTIR and FT-Raman spectroscopies. *Journal of Molecular Structure*, *349*, 349–352.

Spiridon, I., Teaca, C.-A., & Bodirlau, R. (2011). Preparation and characterization of adipic acid-modified starch microparticles/plasticized starch composite films reinforced by lignin. *Journal of Materials Science*, *46*, 3241–3251.

Tomasik, P., & Schilling, C. H. (2004). Chemical modification of starch. *Advances in Carbohydrate Chemistry & Biochemistry*, *59*, 175–403.

Tu, A. T., Lee, J., & Milanovich, F. P. (1979). Laser-Raman spectroscopic study of cyclohexaamylose and related compounds; spectral analysis and structural implications. *Carbohydrate Research*, *76*, 239–244.

Wang, N., Yu, J., Chang, P. R., & Ma, X. (2008). Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydrate Polymers*, *71*, 109–118.

Wang, N., Yu, J., Ma, X., & Wu, Y. (2007). The influence of citric acid on the properties of thermoplastic starch/linear low-density polyethylene blends. *Carbohydrate Polymers*, *67*, 446–453.

Wang, X. L., Yang, K. K., & Wang, Y. Z. (2003). Properties of starch blends with biodegradable polymers. *Journal of Macromolecular Science Part C: Polymer Reviews*, *43*, 385–409.

Wollerdorfer, M., & Bader, H. (1998). Influence of natural fibres on the mechanical properties of biodegradable polymers. *Industrial Crops and Products*, *8*(2), 105–112.

Woodhams, R. T., Thomas, G., & Rogers, D. K. (1984). Wood fibers as reinforcing fillers for polyolefins. *Polymer Engineering and Science*, *24*, 1166–1171.

Zhang, F., Endo, T., Qiu, W., Yang, L., & Hirotsu, T. (2002). Preparation and mechanical properties of composite of fibrous cellulose and maleated polyethylene. *Journal of Applied Polymer Science*, *84*, 1971–1980.