

Green Composites Comprising Thermoplastic Corn Starch and Various Cellulose-Based Fillers

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Starch microparticles (SM) were prepared by delivering ethanol as the precipitant into a starch paste solution dropwise. Chemically modified starch microparticles (CSM) were fabricated by a reaction with malic acid using the dry-preparation technique. Composites were prepared using CSM and various cellulose materials as fillers within glycerol plasticized-corn starch matrix through the casting process. Microcrystalline cellulose (MC, as reference filler) and two cellulose-enriched materials, namely *Asclepias syriaca* L. seed hairs (ASSH) and *Populus alba* L. seed hairs (PSH), were compared in terms of morphology and performance when incorporated within the CSM/S thermoplastic matrix. The effects of cellulose fillers on the morphology, surface, water sorption, and mechanical properties were investigated. The surface water resistance of composite materials was slightly improved through addition of cellulose fillers. Samples containing cellulose fillers presented higher tensile strength but lower elongation values compared with those without fillers.

Keywords: Starch; Cellulose fillers; Composites; FTIR spectroscopy; Mechanical properties

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INTRODUCTION

Green composites based on starch and cellulose polymers can be attractive for different applications such as food packaging and mulch foils, as well as plant pots (horticulture/landscape) (Averous and Boquillon 2004). Starch represents an inexpensive and natural renewable polysaccharide, which has been widely investigated as a substitute for petroleum-derived plastics. Unfortunately, due to the hydrophilic nature of starch, its applications are limited. As a consequence, native starches are often modified through physical or chemical methods to improve their properties and consequently to enhance their application range (Schwartz and Whistler 2009). The main motivations for developing starch-based materials include several advantages (Scott and Gilead 1995) such as flexibility in adjusting the properties to the needs of the specific application by appropriately modifying the composition, low-cost blending as opposed to innovative synthetic material development, and biodegradability.

Chemical modification allows starches to have applications in the non-food industry (*e.g.* as wet-end additives, sizing agents, coating binders, and adhesives in paper industry; as textile sizes; in tableting and cosmetic formulations). Well-known reactions for chemical modification of starch are esterification, etherification, and cross-linking. These included succinylation (Phillips *et al.* 2000), maleination (Chong *et al.* 2001), and acetylation (Phillips *et al.* 1999), which can enhance starch functional value and broaden their range of physico-chemical properties. Chemical modification of starch is commonly carried out in aqueous media, water being considered a green, environmentally friendly

solvent. This approach is used even though the use of water can lead to a relatively low reactivity, a possible reduced selectivity due to side reactions involving water, and also difficulties to be removed.

The chemical modification reactions determine the cross-linking process, which is a common approach to improve the performance of starch for various applications (Huang *et al.* 2007; Wang *et al.* 2010). Determination of the modification degree (Phillips *et al.* 2000) and classification of chemically modified starches using infrared spectroscopy has been described (Dolmatova *et al.* 1998; Dupuy *et al.* 1997).

Starch is not a true thermoplastic polymer, due to its strong inter-molecular and intra-molecular hydrogen bonds, but in the presence of a plasticizer (water, glycerol, sorbitol, *etc.*), high temperature values (90 to 180 °C), and shearing, it melts and fluidizes, enabling its processing in a manner similar to that of synthetic polymers (Curvelo *et al.* 2001). During the thermo-plasticization process, strong interactions between hydroxyl groups of starch molecules are substituted by hydrogen bonds formed between plasticizers and starch, such that the starch becomes plasticized. In the presence of water, the structure of native starch granule is disrupted, breaking the bonds of hydrogen chains, but at the same time, water is acting as a plasticizer (van Soest and Knooren 1997). However, it is necessary to add an additional plasticizer besides water (*e.g.* a polyol) to allow melting to occur below the degradation temperature of the starch (Averous and Boquillon 2004).

Starch modification through acid treatment (mineral or organic) is an efficient method to influence starch properties. Carboxylic acids, for example, can react with starch at room temperature, in the presence of water (*e.g.* formic acid), or do not react in an aqueous medium and require heating to initiate reaction (*e.g.* acetic acid, citric acid). Carboxylic acids were used, besides glycerol and water, to decrease the viscosity of thermoplastic starch by controlling the macromolecules of starch (Carvalho *et al.* 2005).

At high temperature values, water and glycerol are able to physically break up the granules of corn starch and disrupt the hydrogen bonds network, making the native starch plastic. However, starch derivatives resulted from reactions with carboxylic acids are not plasticized through further heating, because substitution of the carboxylic acid groups results in additional dehydration, which cross-linked the starch. Compared with native starch crystals (Putaux *et al.* 2003; Angellier *et al.* 2004; Angellier *et al.* 2006), which can be destroyed through gelatinization process at the high processing temperature, the modified starch is not gelatinized during processing of the films.

The effects of citric acid on the properties of glycerol-plasticized thermoplastic starch were previously investigated (Yu *et al.* 2005), and a decrease of the shear viscosity and improvement in fluidity were observed. The addition of citric acid increased the thermal stability of thermoplastic starch as result of the strong hydrogen-bond interaction between citric acid and starch. The elongation and water resistance were improved, but the tensile stress required for breakage decreased in the presence of citric acid.

Cellulosic materials such as paper, cardboard, wood, agricultural residues, and other fibrous plant materials are in general very widespread and abundant (Demirbas 2005). Cellulose can be obtained from a variety of sources including seed fibers (cotton), wood fibers (from hardwood and softwood species), plant fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valonia ventricosa*), and bacteria (*Acetobacter xylinum*) (Nevell and Zeronian 1985). In its natural state, cellulose is highly crystalline in structure with individual cellulose polymer chains held together by strong hydrogen bonding and van der Waals forces.

The common milkweed (*Asclepias syriaca* L.) is a tall plant containing a milky juice in all of its parts (from which it derives its name). It is native to eastern parts of North America, being naturalized in cultivated ground and dry grassland in various parts of Europe. It is a perennial plant multiplying by seeds and creeping roots that can adapt to adverse soil conditions (e.g. dry and arid, requiring less water).

Natural fibers with higher cellulose content (around 75%), better strength, and higher elongation than those of milkweed floss have been extracted from the milkweed stems (Reddy and Yang 2009). These properties make these fibers suitable for different fibrous applications (e.g. textiles, composites, etc.).

The seeds present lignified silky hairs (floss); these are unicellular and almost colorless, and they are enclosed by a pod. Floss has low density (0.9 g/cm³), unlike any other natural cellulose fibers, and it has short lengths and low elongation. Thus its use for textiles and other applications is limited. Currently, floss mainly is used for comforters.

Common milkweed (*Asclepias syriaca* L.) has been identified as a potential whole-plant source of polyphenols, oil, and hydrocarbons (Campbell 1983). Enzymatic hydrolysis of *Asclepias syriaca* L. seed hairs after pre-treatment in ionic liquids was investigated in a previous study (Spiridon *et al.* 2011a).

Aiming to improve performance or reduce costs for cellulose-based materials, there are many efforts made for investigation upon additional types of fibers. A good example is represented by poplar seed hairs, a cellulose-enriched material present in the biomass waste from *Populus* wood species. This can be considered a valuable resource to be capitalized under environmentally friendly conditions through conversion into useful chemical derivatives or use for different fibrous applications. Poplar seed fibers usually are treated as waste or used as fertilizer. They also can be efficiently used for oil absorbent applications (Likon *et al.* 2013) due to their specific morphology (hollow microtube type) and hydrophobic character (fibers are covered by a waxy coating).

The main objective of the study was to obtain green composites from corn starch and various nonconventional cellulose sources. Previously, corn starch (S) was converted to starch microparticles (SM), which were further reacted with malic acid in order to obtain chemically modified starch microparticles (CSM) according to literature data (Ma *et al.* 2008). These experimental data were presented previously (Spiridon *et al.* 2011b; Bodîrlău *et al.* 2012). CSM were further added to a glycerol-plasticized corn starch thermoplastic matrix. In order to obtain starch–cellulose composite materials, two cellulose-enriched materials, namely *Asclepias syriaca* L. seed hairs (coded as ASSH) and *Populus alba* L. seed hairs (coded as PSH), were used as fillers. Microcrystalline cellulose (coded as MicroCell) was used as a reference sample. The influence of the fillers addition on the morphology, surface properties, and water sorption capacity, as well as mechanical properties of composite materials, was further investigated.

EXPERIMENTAL

Materials

A commercial corn starch (S) was used as the continuous polymer matrix of the composite materials. Glycerol was purchased from Fluka (98% purity, Fluka Chemical, Germany) and used as a plasticizer. Microcrystalline cellulose (MicroCell) powder of high purity was supplied by Sigma-Aldrich, USA. Cellulose-enriched materials, namely *Asclepias syriaca* L. (common milkweed) seed hairs (ASSH) and *Populus alba* L. seeds

hairs (PSH), were obtained from native sources and used without any preliminary treatment (only gentle boiling with distilled water for residue removal). Dried ASSH and PSH were previously fine ground in a Retsch PM 200 planetary ball mill for a good dispersion within composite films. The reagents, ethanol and malic acid, of analytical grade, were provided by Chemical Company, Iasi, Romania. The chemical compositions of ASSH and PSH by comparison with various types of cellulose biomass materials are shown in Table 1 (Spiridon *et al.* 2011a; Pettersen 1984).

Table 1. Composition of Various Types of Cellulose Materials (% Dry Weight)

Cellulose Material	Cellulose	Hemicelluloses	Lignin	Ash
<i>Asclepias syriaca</i> L. seed hairs	54.9	18.0	19.3	0.9
Poplar seed hairs	62.07	-	17.04	2.5
Cotton, flax	80-95	5-20	-	-
Hardwoods	44.3	24.2	21.9	0.6
Softwoods	48.4	8.8	29.0	0.5

Methods

Preparation of starch microparticles (SM) and chemically modified starch microparticles (CSM)

The starch microparticles (SM) and chemically modified starch microparticles (CSM) were prepared according to the literature (Ma *et al.* 2008) with minor modifications. Thus, 10 g corn starch (S) 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 and vigorous stirring. When the resulting starch microparticles (SM) suspensions were cooled to 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 SM were further washed using ethanol to remove the water. After complete washing, these were dried at 50 °C under vacuum to remove the ethanol.

Malic acid (MA) 20 g was dissolved in 100 mL of ethanol. SM (3.5 g) was mixed with 15 mL of malic acid (MA) solution in a glass tray and conditioned for 12 h at room temperature to allow the absorption of MA solution by SM. The tray was dried under vacuum at about 2 mmHg and 50 °C for 8 h to remove the ethanol. The chemically modified starch (CMS) was further 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 MA. CSM mixtures were finally washed with ethanol to remove water, dried at room temperature, and ground. The dried SM and CSM were used for obtainment of composite films using MicroCell, ASSH, and PSH cellulose fillers, respectively.

Preparation of CSM/S/cellulose materials

ASSH and PSH with an average length of 4 ± 1 mm were used for composite samples preparation. CSM 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 0.2 g cellulose filler (ground), resulting in CSM/plasticized starch/cellulose composite materials (CSM/S/cellulose filler) using the doctor blade technique. Table 2 shows the coding of the samples.

Table 2. Code of Starch–Cellulose Composite Samples

Composite Sample	Cellulose Filler
CSM/S	-
CSM/S/MicroCell	Microcrystalline cellulose
CSM/S/ASSH	<i>Asclepias syriaca</i> seed hairs
CSM/S/PSH	<i>Populus alba</i> seed hairs

CSM and cellulose filler loading level (4 wt %) was based on the amount of starch. The mixture was heated at 90 °C for 0.5 h with constant stirring in order to obtain plasticized corn starch.

Composite samples were obtained by dropping and spreading the mixtures 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 composite films were air-cooled and detached from the glass surface to be investigated. Composite samples with a thickness of ~0.2 mm were obtained, this value resulting from measurements by means of a digital micrometer. The starch-based films were pre-conditioned in a climate chamber at 25 °C and 50% RH for at least 48 h prior to the testing. Water content was around 9 wt %.

Fourier Transform infrared (FTIR) spectroscopy

The FTIR spectra of composite materials were recorded by means of a Bruker Vertex 70 spectrophotometer. The spectral resolution was 4 cm⁻¹, and the scanning range was from 400 to 4000 cm⁻¹.

Scanning electron microscopy (SEM)

The morphology of cellulose fillers (ASSH, PSH), as well as that of CSM/S, CSM/S/MicroCell, CSM/S/ASSH, and CSM/S/PSH composite samples was investigated using a scanning electron microscope (FEI QUANTA 200ESEM). Air-dried samples were fixed onto aluminum stubs through carbon-adhesive disks, and their surface was observed with a low-vacuum secondary electron detector using the accelerating voltage of 20.0 kV. The samples were analyzed at room temperature and at an internal pressure of 0.50 torr.

Surface energy evaluation

All contact-angle measurements were performed using an AdveX Instrument at ambient conditions of 22 ± 1 °C and 50 ± 2% RH. In order to characterize the wetting properties, four liquids were used: n-heptane as reference, while water, formamide, and diiodomethane were the wetting liquids. Absorption curves (mass change vs. experiment time) were recorded. All liquids (99%) were provided by Sigma-Aldrich Chemie GmbH (Germany). Contact-angle measurements were used to calculate surface free energy (SFE) values.

Water-uptake measurements

The water absorption was determined (Angles and Dufresne 2000, modified) for all composite materials. The specimens used were thin rectangular strips with dimensions of 20 × 20 × 2 mm. The composite materials were therefore supposed to be thin enough so that the molecular diffusion was considered to be one-dimensional. The samples were first dried overnight at 100 °C. After weighing they were conditioned at 20 °C to 25 °C in a desiccator containing sodium sulfate to ensure an RH ratio of 95%. The conditioning of

samples in a high-moisture atmosphere was preferred to the classical technique of immersion in water, because starch is very sensitive and can partially dissolve after long exposure to water. The samples were removed at specific intervals and weighed. The water content or water uptake of the samples was calculated as follows,

$$\text{Water uptake (\%)} = \frac{M_t - M_0}{M_0} \times 100 \quad (3)$$

where M_t and M_0 are the weights of the sample after t min exposure to 95% RH and before exposure to high moisture content, respectively. The measurements were performed in triplicate.

Opacity

The composite samples opacity was measured with a JENWAY 6405 UV–Vis spectrophotometer and defined as the area under the absorbance spectrum between 400 and 800 nm according to the ASTM D 1003-00 method (ASTM D 1003-00 Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics). The samples were cut into a rectangular piece (1 × 2.5 cm, 0.2 mm thickness), fixed on the inner side of a 1 cm spectrophotometer cell, and the absorbance spectrum was recorded. The composite samples opacity determination was repeated three times.

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. Mechanical testing was done on samples each measuring 10 × 1 cm randomly cut from the cast films. The thickness of each specimen was measured at four points along its length with a digital micrometer. The crosshead speed was 10 mm min⁻¹. A minimum of ten replications of each test sample were run.

RESULTS AND DISCUSSION

FTIR Spectroscopy Analysis

FTIR spectra for composite components (S, SM, CSM, MicroCell, ASSH, and PSH) are presented in Fig. 1. A broad peak at around 3400 cm⁻¹ represents OH groups from starch. This band was displaced to greater wavenumber values for SM and CSM (3424 cm⁻¹ and 3445 cm⁻¹, respectively) (Fig. 1a). The characteristic peak of CSM was located at 1744 cm⁻¹ corresponding to C=O ester carbonyl group stretching (Fig. 1b; Wang *et al.* 2009).

Figures 1c and 1d present the FTIR spectra recorded for MicroCell, ASSH, and PSH. One can observe a broad peak at around 3414 cm⁻¹ assigned to the OH groups from cellulose (Pandey 1999). The peak at around 2918 cm⁻¹ represents the C-H asymmetric stretching in aliphatic methyl. An intense peak appears at around 1734 cm⁻¹ due to ester carbonyl stretching (Fig. 1d). This absorption band mainly arises from the carbonyl stretch in non-conjugated ketone, ester, or carboxylic groups in carbohydrates (hemicelluloses) and not from lignin (Schwanninger *et al.* 2004). The absorbance band at

1734 cm^{-1} in the spectra is most likely attributable to the ester carbonyl group in the xylan component, this peak being more intense for ASSH compared with PSH in concordance with their chemical composition.

The peak at around 899 cm^{-1} is assigned to the β -glycosidic linkage. A band appears at approximately at 1461 cm^{-1} due to the C-H bending vibration of the methylene group.

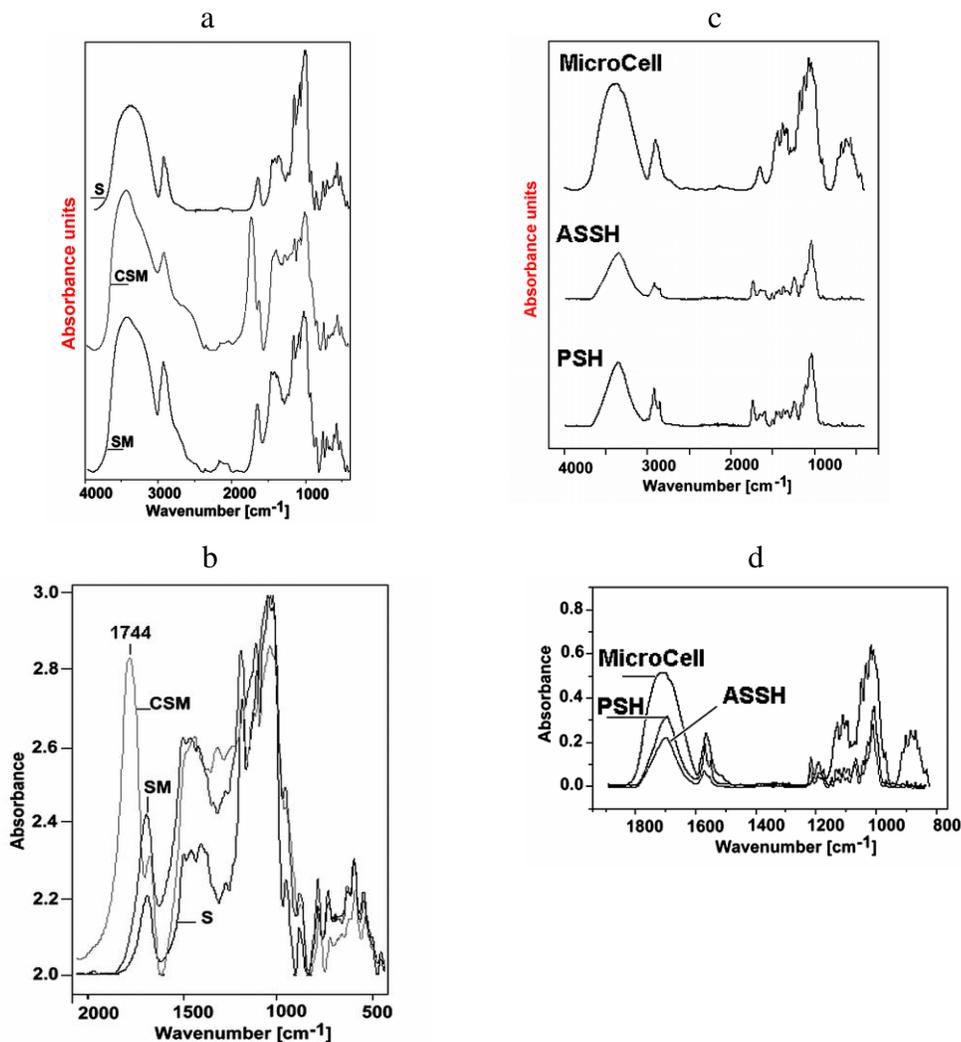


Fig. 1. FTIR spectra recorded for S, SM, CSM, MicroCell, ASSH, and PSH

FTIR spectra recorded for ASSH and PSH differ by comparison with that of the MicroCell spectrum, a fact which reflects the complexity of the cellulose fillers given by their chemical composition (these comprises lignin, hemicelluloses besides cellulose).

Hemicellulose is a natural polymer that is built from not only glucose monomers, but also other monosaccharides such as xylose, mannose, arabinose, and galactose (Johansson 2000). It forms a branched skeleton with an amorphous structure that absorbs water much easier than cellulose. Lignin is a very complex polymer of phenyl–propane units. The presence of lignin is clearly manifested in the FTIR spectra recorded for ASSH, and PSH, respectively (Fig. 1c, d) as bands from 1243 to 1597 cm^{-1} (for AASH), and from 1238 to 1595 cm^{-1} (for PSH), mainly the one at 1508 cm^{-1} , are typical for lignin.

SEM Analysis

The morphology of the obtained composite materials was investigated by SEM. Figure 2 shows SEM micrographs of cellulose fillers (ASSH, Fig. 2a and Fig. 2b; PSH, Fig. 2c and Fig. 2d). Both cellulose fillers exhibited the hollow tubular type form with an external diameter of 9.11 μm (for ASSH), and 5.60 μm (for PSH), respectively, and an average tube wall thickness of 618.5 nm (for ASSH), and 688.6 nm (for PSH), respectively.

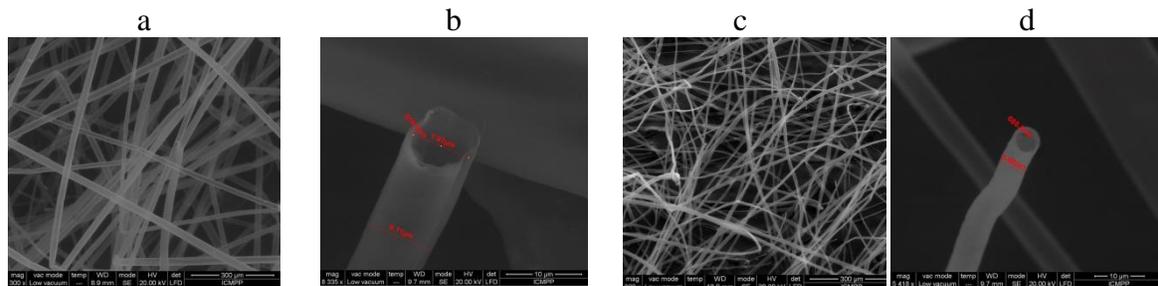


Fig. 2. SEM micrographs for ASSH $\times 300$ (a), $\times 8335$ (b), and for PSH $\times 300$ (c), $\times 5418$ (d)

Figure 3 presents SEM micrographs for starch–cellulose composite materials. As shown in Figs. 3a through 3c, no residual granular structure of corn starch was observed within the continuous glycerol plasticized–corn starch phase. At high temperatures, water and glycerol are known to physically break up the granules of corn starch and disrupt inter-molecular and intra-molecular hydrogen bonds and make the native starch plastic. Substitution of MA groups on starch chains could form a cross-linked starch, limiting starch chain mobility.

The MicroCell, ASSH, and PSH fillers seemed to be better coated by the plasticized starch matrix. This effect is related to the morphology of the filler. Because cellulose fillers have a more uniform shape, these are easier to coat with a softened thermoplastic, such as plasticized starch, during obtainment of the composites. The even and relatively uniform distribution of the fillers in the matrix could play an important role in improving the mechanical performance of the studied composites, as discussed later.

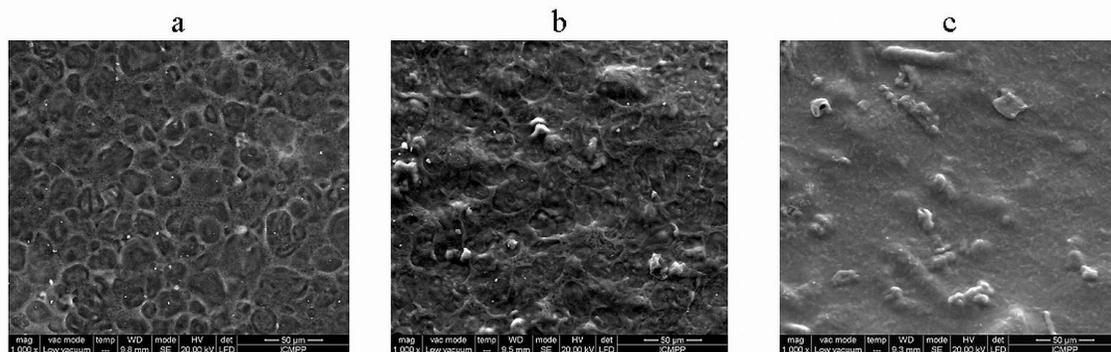


Fig. 3. SEM micrographs for CSM/S/MicroCell $\times 1000$ (a), CSM/S/ASSH $\times 1000$ (b), and CSM/S/PSH $\times 1000$ (c)

The addition of fillers to the composite materials seemed to slightly increase the roughness of the surface, creating a less homogeneous surface (as seen in Fig. 3a, b, and c). A relatively good dispersion and alignment tendency of the cellulose filler within the

composite material was observed due to the lower loading level, the amount of thermoplastic being larger than that of the cellulose material in weight.

Surface Energy and Contact Angle Evaluation

The contact-angle measurement is a traditional method to characterize the hydrophobic or hydrophilic character of composite materials. Experimental data obtained for the composite materials under study are given in Table 4.

Table 4. Total Surface Energy and Contact Angle in Different Liquids of Composite Samples

Composite Sample	Total Surface Energy (mJ/m ²)	Contact Angle in Different Liquids (°)		
		Water	Formamide	Diiodomethane
CSM/S	52.67	55.36±0.45	20.04±0.49	41.13±0.65
CSM/S/MicroCell	47.94	58.32±0.35	32.16±0.37	49.56±0.82
CSM/S/ASSH	40.65	65.95±0.61	53.03±0.32	40.13±0.10
CSM/S/PSH	38.74	68.93±0.53	55.28±0.30	46.49±0.78

From Table 4, one can see that the contact angle of composite materials increased with the addition of cellulose fillers within the plasticized starch matrix. This behavior corresponded to hydrophobic characteristics of the cellulose fillers by comparison with hydrophilic properties of starch, and the results correlated with the decrease of the composite samples surface energy. The addition of cellulose fillers decreased the samples' surface tension values compared with the sample containing only starch (CSM/S).

Water Absorption Measurement

Water sensitivity is an important parameter that determines the usefulness of starch-based biopolymers, starch being known to affect the dimensional stability and the mechanical properties of these materials. Water absorption is often used to study moisture transport through composite materials. Figure 4 shows the water absorption of the starch–cellulose composite materials as a function of time. It was observed that the water absorption of CSM/S/PSH composite was lower than that of the CSM/S composite, at an environmental relative humidity of 95%. These results indicated that the addition of PSH slightly improved the water resistance of the composite material. This trend is in agreement with other reported studies (Curvelo *et al.* 2001) that have associated this behavior with the lower ability of the cellulose fibers to absorb water.

The reason could be that the starch is able to form hydrogen bonds with the hydroxyl group of the cellulose macromolecules, and this strong structure could reduce the diffusion of water molecules in the composite samples. Thus, the combination of cellulose filler with starch may improve water resistance to a certain degree since, as is already known, cellulose is a hydrophilic material, although this feature is more reduced than for that of starch. Similar results were obtained by other researchers, who observed a reduction in the water absorbed by polymer blends and composites made with the addition of cellulose fibers (Ban *et al.* 2006) and hemicelluloses (Gaspar *et al.* 2005) to a starch matrix.

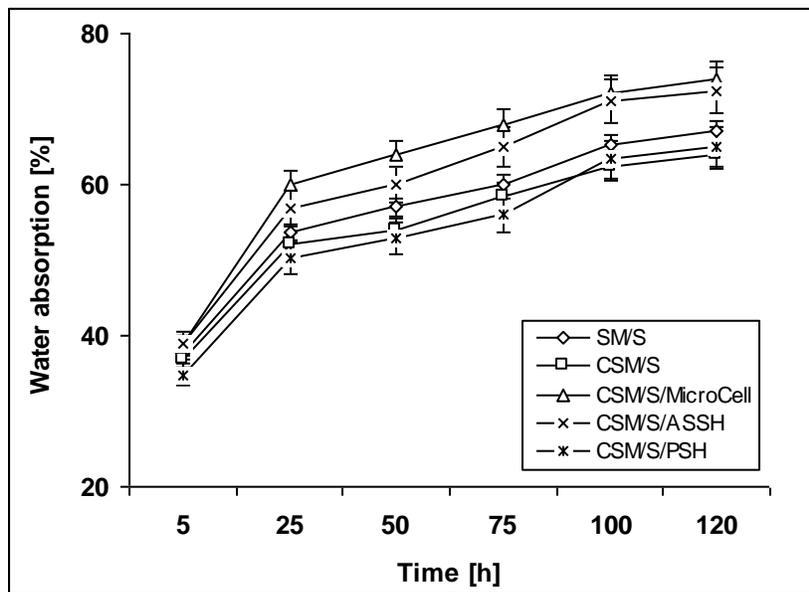


Fig. 4. Water absorption of starch–cellulose composite materials as a function of time

As shown in Fig. 4, water uptake increased up to 90 h. Water absorption values registered for composites comprising cellulose fillers were lower than for that of the samples without filler. This could be due to the starch–cellulose fibers' interactions and to the higher hydrophobic character of the cellulose materials, linked to their crystalline character and the presence of hemicelluloses (mainly xylan) in composition. The more compacted resulting structure reduces the diffusion of water molecules within the composite materials. The results are in concordance with the work of Dufresne and Vignon (1998), who used cellulose microfibrils as a cheap and environmentally friendly filler to provide thermal stabilization and decrease the water uptake of starch-based materials. The amount of modified starch microparticles (CSM) within the polymer matrix may have had some role in the decrease in water uptake of the obtained composite materials (Bodîrlău *et al.* 2012).

Opacity of Composite Materials

Opacity is a very important characteristic for composite materials with applications in food packaging or food coating (Mali *et al.* 2004; Gontard *et al.* 1992), providing information on the size of dispersed particles within the plasticized starch matrix. Thus, opaque composite materials result when the particle sizes are somewhat smaller than the wavelength of visible light under consideration, leading to a high efficiency of light scattering. Figure 5 illustrates the influence of cellulose fillers on the transparency of starch–cellulose composite materials. When light interacts with the composite sample surface, it is reflected, absorbed, or transmitted, and as a result certain values of color, gloss, and transparency are exhibited by the surface. The diffuse reflection of light (known also as light scattering) occurs at the interface of the different polymer components and greatly impairs the light transmission. Cellulose fillers, as water-insoluble polymers, are randomly dispersed within the starch matrix, existing as a discontinuous phase in composite samples after the drying process (Ban *et al.* 2006). Overall, starch–cellulose composite materials remain relatively transparent.

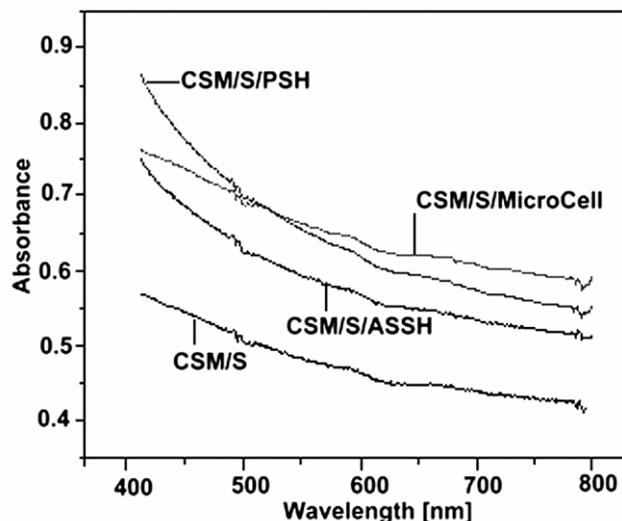


Fig. 5. Opacity values recorded for the starch–cellulose composite materials

The opacity may be affected by various factors, including composite samples' thickness. The addition of cellulose fillers coincided with a marked increase in the area under the curves showing an increase in composite materials opacity. It could be that the samples comprising cellulose fillers exhibit a degree of intra- and inter-molecular regularity to a higher extent than the starch composite sample (CSM/S). The opacity of the composite materials decreases following this order: CSM/S/MicroCell > CSM/S/PSH > CSM/S/ASSH > CSM/S.

Mechanical Testing

Reported information in the technical literature concerning the overall mechanical behavior of composites, which may be used in different domains (*i.e.* for agricultural applications), but also of partially biodegradable composite material, is rather limited. The mechanical behavior of various types of starch-based composite materials is shown to depend, mainly, on their chemical composition and the compounds rate.

The mechanical properties (Young modulus, tensile strength, and elongation at break) of the studied materials are presented in Table 5. Tensile strength and Young's modulus values of composite samples are related to a large extent to the nature of polymer matrix and the adhesion between cellulose fillers and plasticized polymer matrix (Angles and Dufresne 2001). The CSM/S sample evidenced a Young's modulus value of 1158.0 MPa and a tensile strength value of 11.0 MPa. With addition of ASSH and PSH fillers, an increase of tensile strength values were observed, this evolution being related to a good distribution of the fillers given by an adequate interfacial bonding with the plasticized starch matrix (Angles and Dufresne 2001). The Young's modulus of the composite materials significantly increased with MicroCell addition, and this indicated that there was some compatibility between the plasticized starch matrix and the MicroCell filler (which is pure cellulose), and this compatibility was reflected in the performance (*e.g.*, mechanical properties). All these facts were also evidenced by SEM analysis (see Fig. 3).

The use of cellulose fillers (ASSH, PSH), comprising also lignin and hemicelluloses, induces variation of the properties, due to the formation of a three-dimensional network between the different carbohydrates through hydrogen bonds (Dufresne and

Vignon 1998; Dufresne *et al.* 2000). Thus, values of Young's modulus for composite samples comprising AASH and PSH were lower compared with that of a sample with pure cellulose (MicroCell) in composition, which presented a more strongly hydrogen bonded network given by chemical similarity between starch and cellulose.

Table 5. Mechanical Properties of Composite Materials

Composite Sample	Young Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
CSM/S	1158.0 ± 0.33	11.0 ± 0.14	6.7 ± 0.19
CSM/S/MicroCell	1877.6 ± 0.28	33.5 ± 0.21	3.7 ± 0.14
CSM/S/ASSH	887.3 ± 0.36	19.0 ± 0.13	5.3 ± 0.11
CSM/S/PSH	1034.4 ± 0.19	17.4 ± 0.28	4.1 ± 0.12

The tensile strength and elongation at break of the composite materials were inversely related. Thus, the tensile strength value increased with the addition of cellulose fillers (MicroCell, ASSH, PSH), probably due to the interaction between the starch matrix and filler due to their chemical similarity (polysaccharide structure). This more-compacted structure could explain the increase in tensile strength, mainly for the CSM/S/MicroCell sample. The differences registered for tensile strength of samples comprising cellulose fillers could be associated with filler morphology.

Elongation at break is an indication of the films' flexibility and stretching ability. As one can see in Table 6, the starch matrix is more or less rigid, without much possibility for extension. Thus, the elongation decreased from 6.7% for CSM/S to 4.1% for the CSM/S/PSH sample. It is possible that the presence of cellulose fillers within the starch matrix might contribute to the occurrence of heterogeneities in the film structure, with discontinuities. This would result in a decrease of the elongation at break of composites comprising cellulose fillers, which is in agreement with earlier reports on starch-glycerol composites containing different reinforcements (Müller *et al.* 2009; Ma *et al.* 2005). This effect was more significant with MicroCell addition, probably due to its chemical structure similarity with starch, which allows a strong hydrogen bonding interaction within the plasticized starch matrix. All cellulose fillers, but especially MicroCell, enhanced the tensile strength due to their influence on the physical joints in the composite structure, but the cellulose decreased the flexibility of starch polymer chains, with effects on the elongation at break.

CONCLUSIONS

1. Starch reinforced by cellulose is a typical example of a natural polymer composite. In the present study, corn starch as modified microparticles within a plasticized starch matrix (CSM/S) was used to obtain composite materials comprising various cellulose fillers (microcrystalline cellulose as reference, MicroCell; and non-conventional enriched-cellulose sources, namely *Asclepias syriaca* seed hairs, ASSH; and poplar seed hairs, PSH; respectively).
2. The surface properties, water resistance, opacity, and mechanical properties testing (Young's modulus, tensile strength, and elongation at break) of the composite materials under study were investigated. A relatively good dispersion and alignment tendency of the cellulose fillers within the composite material was observed, the

amount of thermoplastic starch being larger than that of the cellulose filler in weight. The transparency of composite materials was reduced through the addition of cellulose fillers (MicroCell, ASSH, and PSH) within the plasticized starch-based polymer matrix. Water resistance of the composite samples was slightly improved to some extent by the addition of cellulose fillers within the starch-based polymer matrix.

3. Tensile strength and Young's modulus values were significantly related to the nature of polymer matrix and the adhesion between cellulose fillers and the plasticized starch-based polymer matrix. All cellulose fillers, but specially MicroCell, which is pure cellulose, enhanced the tensile strength, providing evidence of a better distribution of the fillers (fact evidenced also by SEM analysis), but decreased the flexibility of starch polymer chains in composites, with effects on the elongation at break.
4. Young's modulus values for composite samples comprising AASH and PSH were reduced compared with that of sample with pure cellulose (MicroCell). This fact can be related to the chemical similarity between starch and cellulose which allows more hydrogen bonding interactions within the composite structure.

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