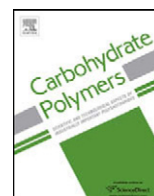




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# Effect of cellulose reinforcement on the properties of organic acid modified starch microparticles/plasticized starch bio-composite films

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### ARTICLE INFO

#### Article history:

Received 29 October 2011  
Received in revised form 8 August 2012  
Accepted 8 October 2012  
Available online xxx

#### Keywords:

Starch  
Cellulose  
Bio-composite  
Thermal properties  
Mechanical testing  
Water resistance

### ABSTRACT

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.

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### 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; Savadkar & 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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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<sup>2</sup>, 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:  $d(0.1) = 230.221 \mu\text{m}$ ,  $d(0.5) = 533.755 \mu\text{m}$  and  $d(0.9) = 1017.174 \mu\text{m}$ . 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  $0.067 \pm 0.005$ .

### 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 K $\alpha$  radiation at 60 kV and 50 mA, at room temperature. Scattered radiation was detected in the diffraction angle  $2\theta$  ranging from 10 to 30° at a rate of 2° min<sup>-1</sup>.

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