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Starch-based nanocomposites: A comparative performance study of cellulose whiskers and starch nanoparticles

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ABSTRACT

A comparative performance study of cellulose whiskers (CW) and starch nanoparticles (SN) on plasticized starch (PS) reinforcement has been presented. In order to study the involved surface phenomena, CW and SN were extracted through acid hydrolysis using sulfuric acid to fulfill the similar surface groups and interactions. CW-filled and SN-filled nanocomposites were then prepared with relatively identical process to alleviate the effect of fabrication method for better comparison of CW and SN performance on PS reinforcement. Morphology of nanoparticles and their dispersion state in the corresponding nanocomposites were investigated by transmission electron microscopy and field emission scanning electron microscopy, respectively. X-ray diffraction was used for crystallography of nanocomposites and established the transcrystallization only in CW-filled nanocomposites. Nanocomposites comprising quasi-spherical SNs showed higher reinforcement in dynamic mechanical tests compared to the corresponding nanocomposites containing rod-like CWs, which were attributed to more efficient filler/filler and filler/matrix interactions originated from hydrogen bonding in SN-filled nanocomposites.

1. Introduction

Starch is produced by most green plants as an energy store and is the most common carbohydrate in human diets and animal foods (Le Corre, Bras, & Dufresne, 2010). This biopolymer has also found many important industrial applications and accordingly huge amount of production. Bio-based and biodegradable products from starch have raised a tremendous level of attention in the recent years, since sustainable development policies tend to expand with the decreasing reserve of fossil fuel and the growing concern for the environment (Angles & Dufresne, 2001). In the molecular level, starch is a heterogeneous material with two architectures. Amylose is a linear structure of α-1,4 linked glucose units, while amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds (Yao, Zhang, & Ding, 2002). Native starch is biosynthesized in the form of semi-crystalline granules made of these two components. Semi-crystalline structure of granules originates from amylopectin chains in double helical configurations (Wang & Copeland, 2013). Starch is not really a thermoplastic but can be converted to a continuous entangled polymeric phase with the aid of water or a nonaqueous plasticizer such as glycerol. Hence, the obtained material can be processed by technologies developed for synthetic polymers (Angellier, Molina-Boisseau, Lebrun, & Dufresne, 2005). In practice, plasticized starch (PS) shows a limited physical performance (Teixeira et al., 2009), so must be reinforced to achieve satisfactory mechanical properties. Various methods that have been used to reinforce PS can be categorized in three main categories: (1) chemical treatment of starch molecule (Avérous, 2004; Cao & Zhang, 2005a, 2005b), (2) mixing PS with other natural or synthetic polymers (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Avérous, 2004) and (3) using various natural and mineral reinforcers.

Mineral fillers such as talc (Bhatnagar & Hanna, 1996), kaolin (de Carvalho, Curvelo, & Agnelli, 2001) and clay (Wilhelm, Sierakowski, Souza, & Wypych, 2003) and natural reinforcers including plant fibers from different sources (Curvelo, de Carvalho, & Agnelli, 2001), cellulose microfibers (Chen, Cao, Chang, & Huneault, 2008; Dufresne & Vignon, 1998), cellulose whiskers (CWs) (Cao, Chen, Chang, Muir, & Falk, 2008; Teixeira et al., 2009) and starch nanoparticles (SNs) (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Viguié, Molina-Boisseau, & Dufresne, 2007) were utilized to reinforce PS up to now. Retaining PS biodegradability and exploiting nanoparticle exclusive properties (such as high modulus and high surface/weight ratio) have increasingly promoted the usage of natural nano-reinforcers in the recent years (Angles & Dufresne, 2001). In addition, chemical similarity of matrix and reinforcer leads to an efficient interface and facilitate stress transfer from matrix to the reinforcer, which improves the final performance of the

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composite (Viguié et al., 2007). Therefore, due to the chemical similarity of CWs and SNs with starch based matrix, they have been suggested as promising candidates for PS reinforcement. One of the first studies in PS reinforcement by CWs was reported by Angles and Dufresne (2000, 2001). They showed that due to the accumulation of PS plasticizers on the nanoparticle surfaces, starch molecular movements are facilitated and crystallization of starch chains on the CW surfaces (transcrystallization) occurs. The formation of this soft interphase has been shown to disturb the stress transfer from matrix to fibers and interfere with inter-whisker hydrogen bonding, which leads to decreased final mechanical performance of the nanocomposite (Angles & Dufresne, 2000, 2001). In another study, Teixeira et al. (2009) used cassava bagasse cellulose nanofibrils to reinforce PS and attributed the deficiency of nanoparticles in expected improvement of mechanical properties to transcrystallization. Angellier et al. (2006) studied the reinforcement of waxy maize starch with nanoparticles extracted from the same material. They investigated various factors including glycerol and filler content and aging in different relative humidity on PS mechanical properties. They ascribed the reinforcing effect of nanoparticles to powerful particle/particle and particle/matrix interactions arose from the hydrogen bonding. Viguié et al. (2007) studied the impact of waxy corn SNs on waxy corn PS mechanical properties. They reported 22 times increase in matrix tensile modulus after inclusion of 25 weight percent (wt%) of reinforcer, which was correlated with the powerful interface as a result of hydrogen bondings. García, Ribba, Dufresne, Aranguren, and Goyanes (2009) evaluated the effect of waxy corn SNs in the reinforcement of cassava PS. They related 380% increase of rubbery storage modulus in the presence of 2.5 wt% of SNs to the powerful hydrogen bonding between matrix and particles and among particles themselves. Le Corre et al. (2010), comparing CWs and SNs in PS reinforcement, indicated that the positive impact of SNs in the PS mechanical behavior is more significant than that of CWs. This result is surprising since CWs appear as rod like nanoparticles with the high aspect ratio that should provide a higher reinforcing capability than quasi-spherical starch particles (Angellier et al., 2006). This apparent controversy reveals the need for more precise investigation of the involved factors in reinforcement of PS nanocomposites.

Ishida and Bussi (1991) and recently Li and Yan (2011) have reviewed literatures about transcrystallization in the presence of micro- and nano-scale fibers. They mentioned some factors include similarity in chemical structure and crystalline network of fiber and matrix as the main factors in this phenomenon. Generally, macroscopic properties of starch based nanocomposites are related to reinforcer aspect ratio, fabrication method and filler/filler and filler/matrix interactions (Samir, Alloin, & Dufresne, 2005). Accordingly, similar fabrication procedure can help the precise evaluation of two other remaining factors.

Owing to structural similarity with the matrix, cellulose whiskers and starch nanoparticles have been chosen for PS reinforcement in the current research. CWs and SNs were extracted through acid hydrolysis using sulfuric acid to fulfill the similar surface groups and interactions among nanoparticles and also with the matrix. CW-filled and SN-filled nanocomposites were then prepared with relatively identical process in order to alleviate the effect of fabrication method for better evaluation of CWs and SNs performance and the involving surface phenomena on PS reinforcement. After morphological investigation and crystallography of nanocomposites, their reinforcement efficiency were investigated by dynamic mechanical thermal analysis (DMTA), and then efficiency of nanoparticles on PS reinforcement was scrutinized based on particle/particle and particle/matrix interactions and surface phenomena.

2. Materials and methods

2.1. Materials

Food-grade wheat starch (from Kerman, Iran) containing about 27% amylose and hygiene cotton fibers were used in this study. Glycerol (98%) and sulfuric acid (98%) were supplied by Dr. Mojallali Chemical Company.

2.2. Cellulose whisker extraction

CWs were extracted from cotton fibers by Roohani et al. (2008) method. Firstly, 5 g cotton fibers were finely chopped. Chopped fibers were then added to 64 wt% sulfuric acid aqueous solution (fibers per solution ratio 1/20). Acid hydrolysis of cotton fibers were carried out at 45 °C under vigorous mechanical stirring (700 rpm) for 45 min. Then, the ensuing suspension was diluted with cold distilled water and neutralized by centrifugation and dialysis against distilled water. After dialysis, the suspension pH reached 6–7. In order to achieve individual particles, the resulting suspension was submitted to an ultrasonic treatment for 10 min in an ice bath. For the direct use in the nanocomposite preparation, resulting suspension was concentrated to more than 5 wt% in a moderate temperature under slow stirring and was stored in the refrigerator. The concentration of suspension was precisely measured by completely drying a certain amount of it (5 g) and calculating the weight difference before and after drying.

2.3. Starch nanoparticle extraction

SNs were extracted from wheat starch based on Angellier, Choisnard, Molina-Boisseau, Ozil, and Dufresne (2004) method. Briefly described, 36.725 g starch was mixed with 250 ml of 3.16 M aqueous solution of sulfuric acid and stirred vigorously (400 rpm) for 5 days at 40 °C. The resultant suspension was then diluted with cold distilled water and neutralized by centrifugation and dialysis against distilled water. After dialysis, the suspension pH reached 5–7. In order to achieve individual particles, the resulting suspension was submitted to an ultrasonic treatment for 5 min in an ice bath. For the direct use in the nanocomposite preparation, resultant suspension was concentrated to more than 5 wt% in a moderate temperature under slow stirring and was stored in the refrigerator. The concentration of suspension was precisely measured by completely drying a certain amount of it (5 g) and calculating the weight difference before and after drying.

2.4. Starch matrix preparation

To prepare the matrix, 3 g starch was first dispersed in the mixture of 1.5 g glycerol and 25.5 g distilled water. The gelatinization was performed in a 100 m two-necked glass reactor under vigorous stirring (200 rpm) at 120 °C for 30 min. After mixing, the resulting suspension was casted in a glass Petri dish and dried in a vacuum oven at 50 °C for 24 h.

2.5. Nanocomposite preparation method

PS nanocomposites containing 10, 15 and 20 wt% of nanoparticles based on the total weight of starch and glycerol (Nanoparticle/starch + glycerol) were prepared according to the following procedures.

2.5.1. Cellulose whisker-filled nanocomposites

Cellulose whisker suspension containing predetermined amount of particles was diluted until its water content reached 25.5 g. To ensure the homogeneity, suspension was submitted to