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Novel nanocomposites based on fatty acid modified cellulose nanofibers/poly(lactic acid): Morphological and physical properties

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ABSTRACT

A novel poly(lactic acid) (PLA) based nanocomposite, reinforced by cellulose nanofibers (CNFs) was prepared. CNFs were previously treated by oleic acid for improving the compatibility with PLA matrix. Resulted modified nanofibers (MCNFs) exhibited reduced surface polarity in comparison to non-modified CNFs. MCNFs were subsequently introduced into PLA matrix and the effects of the CNFs surface modification on morphological, mechanical, thermal and barrier properties of the PLA based nanocomposites were studied. The morphology of fracture surfaces was evaluated by field emission scanning electron microscopy (FE-SEM). Differential scanning calorimetry (DSC) showed that the melting temperatures of the PLA–MCNF nanocomposites were considerably higher than that of the pure PLA film. The ultimate tensile strength and Young's modulus of nanocomposites (at 12% MCNFs) were about 2.5 and 2 times as much as those of the pure PLA films, respectively. In addition, adding MCNFs caused a decrease in water vapor permeability.

1. Introduction

Over the last decades, biopolymers have received an increased interest due to growth of environmental concerns, increased price of crude oil and global warming (Vroman & Tighzert, 2009). Poly(lactic acid) (PLA) is one of the most studied biodegradable polymers, which has greatly attracted interests due to its unique properties and renewability. PLA is a linear aliphatic thermoplastic polyester with some good properties such as high biodegradability, mechanical stiffness, clarity, gloss, and UV stability. However, range of PLA applications is still limited by some shortcomings such as its brittleness, low thermal stability and poor barrier properties, which may be

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Abbreviations: PLA, poly(lactic acid); CNF, cellulose nanofibers; MCNF, modified cellulose nanofibers; OLA, oleic acid; SEM, scanning electron microscopy; FE-SEM, field emission scanning electron microscopy; DSC, differential scanning calorimetry; WVP, water vapor permeability; FTIR, Fourier transform infrared; XRD, X-ray diffraction; TGA, thermogravimetric analysis.

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improved by adding reinforcing compounds (fillers) and forming composites (Jamshidian, Arab Tehrany, Imran, Jacquot, & Desobry, 2010; Suprakas, Pralay, Masami, Kazunobu, & Kazue, 2002). Most reinforced materials show poor matrix–filler interactions, which tend to improve with decreasing filler dimensions. The use of fillers with at least one nanoscale dimension (nanoparticles) produces nanocomposites. Nanoparticles have proportionally larger surface area than their microscale counterparts, which favors the filler–matrix interactions and the performance of the resulting material (Sorrentino, Gorrasi, & Vittoria, 2007). In order to produce fully renewable and biodegradable nanocomposites, both the polymer matrix and the nano-filler have to be derived from renewable resources. Cellulose nanofibers (CNFs) have attracted interests during the last decade as potential nano-reinforcing materials in different polymers due to their appealing intrinsic properties including nanoscale dimensions, high surface area, low density and high mechanical strength, renewability and biodegradability (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Habibi, Lucia, & Rojas, 2010).

Hence, CNFs have been evaluated in terms of reinforcing different polymeric matrices like starch (Kaushik, Singh, & Verma, 2010), polyvinyl alcohol (Ibrahim, El-Zawawy, & Nassar, 2010), poly(lactic acid) (Dobreva et al., 2010; Nakagaito, Fujimura, Sakai, Hama, & Yano, 2009), poly(vinyl chloride) (Chazeau, Paillet, & Cavaille, 1999) and other polymers (Cherian et al., 2011; Xu, Kawata, Hosoi, Kawai, & Kuroda, 2009). The properties of fiber-reinforced composites are strongly influenced by interactions between the components. The major problems of researchers in this field are mostly related to the highly polar surface of the cellulose fibers, which causes a very low interfacial compatibility with non-polar polymer matrices, moisture uptake and inter-fiber aggregation by hydrogen bonding (Cunha & Gandini, 2010). Several strategies have been accomplished to overcome these drawbacks such as esterification (Matsumura, Sugiyama, & Glasser, 2000), silylation (Gousse, Chanzy, Cerrada, & Fleury, 2004; Gousse, Chanzy, Excoffier, Soubeyrand, & Fleury, 2002) and acetylation (Hu, Chen, Xu, & Wang, 2011; Ramos, Morgado, El Seoud, da Silva, & Frollini, 2011). These modifications are mostly involved specific surface treatments of the fibers for decreasing the CNFs hydrophilicity.

Over last years, the production of the PLA based nanocomposites by using different modified cellulose nano-fibers have been reported by several research groups (Bondeson & Oksman, 2007; Frone, Berlioz, Chailan, & Panaitescu, 2013; Lin, Chen, Huang, Dufresne, & Chang, 2009; Petersson, Kvien, & Oksman, 2007; Yu, Ren, Li, Yuan, & Li, 2010). Huda, Drzal, Mohanty, and Misra (2008) studied the effect of fiber surface-treatment on the properties of laminated PLA/kenaf fiber composites. Their results showed that both silane-treated and alkali treated fibers had more reinforcing effects on mechanical properties of composite in comparison to non-treated fiber. Lin, Huang, Chang, Feng, and Yu (2011) reported that the nanocomposites based on PLA-acetylated CNF_S showed considerable higher tensile strength and lower elongation at break in comparison to pristine PLA. Meanwhile, the crystallinity and melting temperature of the composites were elevated probably due to the nucleation effect of CNFs.

A well-known innovative way to prepare green cellulose based fillers for polymeric composites is the esterification of cellulose by fatty acids because fatty acids are renewable and biodegradable materials (Freire, Silvestre, Pascoal Neto, Belgacem, & Gandini, 2006). They are typically attached covalently to the surface of cellulose by an esterification reaction via acylation (Uschanov, Johansson, Maunu, & Laine, 2011). To our knowledge, this reaction has not been exploited for the modification of softwoods CNFs. This type of CNFs has the highest aspect ratio, and the lowest fiber cross section compared to other types of CNFs (Gindl & Keckes, 2005). Furthermore, to the best of our knowledge, there is no report on the preparation of PLA/fatty acid modified CNF nanocomposites and the current research is the first report on the using of oleic acid modified cellulosic nanofibers as reinforcing agent in the polymeric materials.

In this work, the surfaces of CNFs were chemically modified by oleic acid (OLA) for providing modified cellulose nanofibers (MCNFs). It was hypothesized that esterification could potentially improve the hydrophobicity of CNF which in turn would promote miscibility and interfacial adhesion with the PLA matrix, ultimately enhancing mechanical performance, thermal stability and barrier properties of the resultant composites. So that, the purpose of the present research work was to study the effect of the OLA modified CNFs on the morphological, mechanical, thermal, and barrier characteristics of PLA based film.

2. Materials and methods

2.1. Materials

Poly(lactic acid) (PLA) 2.4100.CL (M_w = 140,000) was purchased from FKuR Kunststoff GmbH (Germany); cellulose nanofibers (CNFs) prepared from softwood that were kindly provided by Nano Novin Polymer Co. (Iran). The main characteristics of CNFs used in this work includes: average diameter ~28 nm, crystallinity ~72% and crystallite size 4.6 nm. The reagents used in CNFs modification were pyridine (Py; Merck), p-toluenesulfonyl chloride (TsCl; Sigma–Aldrich) and oleic acid (OLA; Sigma–Aldrich). Chloroform, diiodomethane, calcium sulfate and potassium sulfate (analytical grade) were purchased from Merck (Darmstadt, Germany).

2.2. Surface modification of CNFs

Preparation of partially esterified or modified CNFs (MCNFs) by OLA in a Py/TsCl system followed the procedure discussed by Shimzu and Hayashi (1989). CNFs (0.5 g) were added to a 250 ml two-necked flask, containing a solution of Py (15 ml) and TsCl (3.5 g), with stirring. The OLA was slowly added to the mixture to give a 1:1 TsCl/OLA molar ratio (~5 g OLA). The temperature of the reaction mixture was kept at 50 °C for 4 h. The product was filtered and washed with methanol and ethanol, then Soxhlet extracted with methanol for 6 h to remove non-reacted fatty acids. Finally the cellulose was filtered, washed with methanol, ethanol, acetone and water and dried at 60 °C.