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Material properties

Preparation and characterization of modified cellulose nanofibers reinforced polylactic acid nanocomposite

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ABSTRACT

Nanocomposites composed of cellulose nanofiber (CNF) and polylactic acid (PLA) were prepared using a solvent casting method, with the goal of making green nanocomposites. Prior to the incorporation of CNF into the polymer matrix, surface modification of CNF was accompanied by esterification to improve the dispersion of CNF and its interfacial adhesion with the biopolymer. Microstructure, barrier, mechanical and thermal properties of the nanocomposites were studied. Scanning electron microscopy (SEM) micrographs revealed uniform distribution of nanoparticles in the polymer matrix at low contents (1 and 3 wt%), but also that a higher content (5 wt%) of CNF was easily agglomerated. This caused the mechanical properties of the nanocomposites to be reduced. The results of water vapor permeability (WVP) tests showed that the use of acetylated nanofibers had no significant effect on the permeability of films. Tensile strength (TS) and elastic modulus (EM) of nanocomposites with 1 wt% CNF did not show significant changes, however elongation percentage (E) increased by more than 60%. The TS, EM and E changed significantly for nanocomposites with 3 and 5 wt% CNF. Moreover, nanofiber orientation effectively occurred in the PLA matrix. The reinforcing effect of CNF composition with PLA caused a slight increase in glass transition and melting temperatures. However, the nanocomposite films showed a very similar pattern of thermal behavior to that of neat PLA film.

1. Introduction

Recently, considerable research effort has been undertaken to develop new plastic materials with low environmental impact. Thermoplastic polymers were compounded with natural materials to reduce the costs of production while maintaining their properties [1]. In particular, composites and nanocomposites of biopolymers with natural fillers seem to be very promising for the development of environmentally friendly materials [2,3]. Biopolymers are naturally occurring polymers that are found in all living organisms. The use of biopolymers has less adverse impact on our environment compared to using fossil fuel based commodity plastics [4]. During the last two decades, considerable attempts have been made to develop biodegradable polymers and composites [3]. Aliphatic polyesters such as polylactic acid (PLA), polycaprolactone (PCL), poly (3-hydroxybutyrate) (PHB) and polyglycolic acid (PGA) represent important biodegradable polymers, which are now finding commercial applications in combination with bio-based materials [5]. PLA, is a linear aliphatic thermoplastic polyester, produced from renewable resources, which has gained much attention in both research and applications [6,7]. This polymer is produced either by ring

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opening polymerization of lactide or by polycondensation of lactic acid monomers. The monomer is obtained from the fermentation of corn or other renewable agricultural raw material [8,9]. Poor thermal and mechanical resistance and limited gas barrier properties compared to petroleum-based polymers are the main limitations for the application of PLA in packaging [10,11]. The above drawbacks could be overcome by enhancing their thermo-mechanical properties through copolymerization, blending and filling techniques. Combining synthetic PLA with natural polymers such as cellulose and starch is a suitable strategy for cost reduction and improvement of combined properties.

Cellulose fiber-reinforced polymer composites have received much attention because of their low density, low cost, non-abrasiveness, fire resistance, lack of toxicity and biodegradable properties. A great deal of research has been done to study the effect of using cellulose fibers as the reinforcing component of different composites [12]. Despite the fact that nanocellulose has great potential as a biological reinforcement in bio-nanocomposites, its uniform dispersion, moisture absorption, quality variations, low thermal stability and compatibility with common polyester matrix in composite materials remain as big challenges. Thus, proper interface compatibilization of the polyester-nanocellulose blends could lead to improvement in those properties. The chemical modification of hydrophilic hydroxyl groups is one of the proposed strategies to reduce the cellulose surface polarity [13–15]. Among the chemical modification methods that can reduce the hydrophilic surface characteristics of cellulose, acetylation is a promising technique [16,17]. Acetylation is a chemical modification, in which the chemical reacts with OH groups in the cellulose, thereby turning the hydrophilic surface of cellulose into a hydrophobic one. In particular, acetylation can improve the hydrophobic characteristics of cellulose surfaces, resulting in better dispersibility in the intrinsic non-polar matrix during further processing [18,19].

Several studies of nanocellulose as reinforcement in PLA have been carried out and the nanocomposites have been prepared by solvent casting as well as melt compounding [18–20]. In a study by Iwatake et al. [21], microfibrillated cellulose (MFC, microfibrillated cellulose, mostly consisting of nanofibers) was used to reinforce polylactic acid (PLA) with the goal of making sustainable ‘green-composites’. In a recent report by Jonoobi et al. [18], the effect of chemical modification of cellulose nanofiber (CNF) on the properties of polylactic acid (PLA) nanocomposites was evaluated. The results showed that the tensile and dynamic mechanical properties of the nanocomposites were enhanced compared to neat PLA matrix.

As regards cellulose-PLA nanocomposites, previously published papers focused on the physical, mechanical or thermal properties of PLA nanocomposites. However, the present study is aimed at a comprehensive assessment of the different functional properties of produced PLA/CNF nanocomposites. The effect of nanofiber loading on the phase morphology, dispersion of nanoparticles, physical, mechanical, thermal and barrier properties of the resulting PLA/CNF nanocomposite films are also investigated in detail.

2. Experimental

2.1. Materials

PLA (Bio-flex®F 6510) was obtained from Fkur kunststoff GmbH (Siemensring 79, Germany) with a density of 1300 kg/m^3, melting point of 150–170 °C and molecular weight of 197,000 g/mol. PLA resins were dried in a vacuum oven at 60 °C for 24 h before use. CNF gel (3 wt%) was supplied by Nano Novin Polymer Co. (Sari, Iran). All other reagents and solvents were of analytical grade and were used without further purification.

2.2. Cellulose acetylation

A mixture of acetic acid (25%) and sulfuric acid (3%) stirred at 70 °C for 30 min was prepared to activate CNF. The acetylation of CNF was performed by adding 10 mL anhydride acetic and 50 mL acetic acid, and then stirring for 4 h at 100 °C. The acetylated CNF were then added to a solution of acetone: methanol (2:1, v:v) and chloroform to fulfill the sequential phase transition of acetylated fibers to chloroform, which could then be adequately mixed with PLA.

2.3. Film preparation

PLA and PLA-based nanocomposite films were prepared using a solvent casting method [22]. In brief, dissolved PLA (5 g) in chloroform (100 mL), was vigorously agitated for 8 h at room temperature (25 °C). The solution was then poured into greased glass molds, followed by drying at room temperature for 24 h. Subsequently, the prepared PLA film was removed from the casting surface. For the preparation of PLA nanocomposite films, a certain amount of CNF was suspended in chloroform under vigorous stirring for 8 h using a magnetic stirrer. The mixed materials were then homogenized at 8000 rpm for 15 min using an ultra turrax T-25 homogenizer (IKA T25-digital ultra turrax, Germany) with a S25N-25F probe, followed by sonication for 30 min at room temperature using a high intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., Newtown, CT, USA). Solutions containing 1, 3 and 5 wt% CNF were added to the previously prepared PLA solution and then stirred vigorously for 15 min with a magnetic stirrer. The solutions were homogenized at 8000 rpm for 15 min and sonicated for another 30 min. The final film was obtained by the same procedure explained earlier for neat PLA films. After drying at room temperature for 24 h, all PLA/CNF films were further dried at 60 °C in a vacuum dryer to remove the remaining solvent (chloroform) to prevent its plasticizing effect [23].

2.4. Morphological study

Studies on the morphology of the composites were carried out using a scanning electron microscope (SEM). SEM micrographs of the fracture surfaces of the specimens after tensile test were taken using a SEM model WEGA-II TESCAN. The specimen was coated with a thin film (100 Å) of gold to avoid electrical charge accumulation