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Material properties

Bionanocomposite based on cellulose nanowhisker from oil palm biomass-filled poly(lactic acid)

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ABSTRACT

Cellulose nanowhiskers (CNW) extracted from plant fibers exhibit remarkable properties that make them suitable for use in the development of bionanocomposites. CNW have demonstrated the capability to enhance the properties of a polymer matrix at low filler loading. In this study, poly (lactic acid) (PLA) bionanocomposites were prepared using the solution casting technique, by incorporating the PLA with the CNW obtained from an oil palm empty fruit bunch (OPEFB). Fourier transform infrared spectroscopy showed no significant changes in the PLA peak positions, which indicates that incorporating the CNW into the PLA did not result in any significant changes in the chemical structure of the PLA. Thermogravimetric analysis, on the other hand, revealed that the bionanocomposites (PLA-CNW) had better thermal stability than the pure PLA. The tensile strength of PLA-CNW increased by 84% with the addition of 3 parts of CNW per hundred resins (phr), and decreased thereafter. Moreover, a linear relationship was observed between the Young's modulus and CNW loading. Elongation at break, however, decreased with the addition of 1-phr CNW, and remained constant with further addition. Transmission electron microscopy revealed that agglomeration of CNW occurred at 5-phr loading, consistent with the tensile strength results. Overall, the CNW obtained from OPEFB can enhance the tensile and the thermal properties of bionanocomposites.

1. Introduction

In recent years, numerous attempts have been made to produce biodegradable polymer composites by using poly(lactic acid)(PLA) [1–3], polyhydroxybutyrate [4], starch [5,6], cellulose [7,8] and poly(hydroxyoctanoate) [9,10] due to their sustainability and environmental friendliness. PLA, however, has been viewed as the most promising candidate in the production of bionanocomposite polymers. PLA is a thermoplastic aliphatic polyester that can be derived from carbohydrate-rich sources, such as corn starch [11–13]. It has been used in packaging industries, and shows good potential for use in automotive materials, as well as biomedical applications, including tissue engineering [11,12,14,15]. Although PLA has attracted researchers' interest as a biodegradable polymer, the applications in which PLA can be used are still limited, due to its low thermal stability, slow degradation and low barrier properties [14,16]. Reinforcement fillers, either micro- or nano-particle, have been incorporated into PLA in order to overcome these inherent shortcomings, while at the same time maintaining its positive attributes, such as transparency and biodegradability [14,17].

Clay is the inorganic nano particle most commonly used in polymeric nanocomposites as a reinforcement agent. In order to produce fully biodegradable nanocomposites, replacing clay with a renewable and sustainable material, such as cellulose, is the best option [14,18]. As the main structural component in the cell walls of all plants, cellulose is water-insoluble, fibrous, easy to modify chemically and mechanically, biocompatible and renewable, with a

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high length-to-diameter (L/d) axis ratio, and widely available. Cellulose demonstrates better mechanical properties compared to those of other inorganic reinforcing fillers [19,20]. Another advantage of cellulose is its high sound attenuation and comparatively easy processing, due to its non abrasive nature, allowing for high filling levels which, in turn, results in significant cost savings [21,22].

The use of cellulose nanoparticles as a reinforced phase in composite production has generated immense interest among researchers [11,23,24]. The principal reasons for the utilization of cellulosic materials are their high specific strength and moduli compared to other engineering materials, and their reinforcing potential [25]. One type of cellulose nanoparticles that has received much attention among researchers is cellulose nanowhiskers (CNW).

CNW have been obtained under controlled conditions that lead to the formation of high-purity single crystals after the removal of amorphous regions. The resultant highly ordered structure produces, not only unusually strong particles, but also significant changes in electrical and optical properties [23]. The tensile properties of CNW are far above the current high-volume content reinforcements, and allow the processing of the highest attainable composite strengths [1,22]. CNW is considered an ideal filler in the development of transparent polymeric materials, since it does not cause light scattering [26]. Pandey et al. [27] reported that the tensile strengths and the Young's moduli of PLA nanocomposites improved with the use of CNW produced from grass. Cho et al. [28] observed that CNW obtained from commercial microcrystalline cellulose (MCC) was able to improve the storage modulus and the biodegradability of the PLA. Studies conducted by Peterson et al. [15] showed that CNW was capable of improving the storage modulus of the PLA at higher temperatures.

The present paper investigates the use of CNW isolated from oil palm empty fruit bunch (OPEFB) microcrystalline cellulose (MCC) by means of the chemical swelling treatment approach. As reported earlier by Haafiz et al. [20], incorporating OPEFB-MCC into the PLA had a negative effect on the mechanical properties of PLA. Therefore, the current study was conducted to evaluate the effect of CNW content derived from OPEFB-MCC on the morphological, thermal and tensile properties of PLA-CNW, with the aim of developing bionanocomposites.

2. Experimental

2.1. Materials

PLA (3001D) in pellet form was supplied by NatureWork® LLC, USA, with a density of 1.24 g/cm^3 and melt flow index (MFI) of approximately 15 g/10 min (190 °C/2.16 kg). Cellulose nanowhiskers (CNW), used as a filler in this study, were obtained from oil palm empty fruit bunch (OPEFB) microcrystalline cellulose (MCC-OPEFB) using the swelling method approach. The isolation and the production of CNW were described in detail earlier [29,30]. Other chemicals, such as chloroform, acetone, *N, N*-dimethylacetamide (DMAc) (99% purity) and lithium chloride (LiCl) (99% purity), were purchased from Merck Malaysia, and used as received.

2.2. Preparation of PLA and PLA-CNW bionanocomposites

A solution of PLA (10 wt%) in chloroform was prepared by stirring the pellets at 60 °C for 2 h until totally dissolved [14]. The solution was then immediately cast onto glass plates and left at ambient temperature for 48 h. The cast PLA, approximately 100 μm thick, was obtained and noted as pure PLA.

For PLA-CNW bionanocomposites, the PLA solution (10 wt%) was mixed with different CNW loading (1, 3 and 5 part per hundred resins (phr)). The mixture was kept at 60 °C under strong agitation until the PLA pellets were fully dissolved. The CNW used in this stage was in suspension form. Therefore, the solvent exchange was performed first, before the CNW was mixed with the PLA. At this stage, water was exchanged with acetone, and then the acetone was exchanged with chloroform. The solvent exchange was done by using a Universal 32 Hettich (Newport Pagnell, England) centrifuge. The solvent-exchanged CNW was then sonicated in a Branson 2510 ultrasonic bath for 5 min, and stirred into the PLA under strong agitation for approximately 2 h. The dissolved PLA containing CNW was then sonicated for another 5 min before casting. The bionanocomposite, approximately 100 μm in thickness, was then obtained through solvent evaporation at room temperature for 48 h prior to analysis. The obtained PLA bionanocomposites were designated as PLA-CNW1, PLA-CNW3 and PLA-CNW5, based on CNW composition.

3. Characterization

3.1. Fourier transforms infrared spectroscopy

Fourier transform infrared (FT-IR) was performed using a Perkin Elmer 1600 Infrared Spectrometer. The samples' spectra were recorded using Nicolet's AVATAR 360 at 32 scans, with a resolution of 4 cm^{-1}, within the wave number range of 4000 to 370 cm^{-1}. The "find peak tool", provided by Nicolet OMNIC 5.01 software, was used to measure the significant transmittance peaks at particular wave numbers.

3.2. Thermogravimetric analysis

A thermogravimetric analyzer (TGA) Model 2050 (TA Instruments, New Castle, DE) was used to characterize the thermal stability of the PLA and the PLA-CNW. The specimens were scanned at temperatures ranging from 30 °C to 600 °C at a rate of 10 °C/min, and analyses were performed under nitrogen gas flow.

3.3. Tensile test

The tensile strength at break for each sample was measured using an Instron 4400 Universal Tester. The tensile test was carried out at room temperature, according to ISO 527-3. A fixed crosshead speed of 12.5 mm/min was used in all cases, and an average of five tests was taken.

3.4. Microscopy analysis

The morphology of samples was observed using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). FESEM was conducted using a FESEM-EDX Oxford INCA 400 model, at an acceleration voltage of 10 kV. The samples were sputter-coated with gold to avoid charging. A TEM model LEOLIBRA was used, and specimens with a thickness of about 60 nm were prepared using a Leica ultracut ultramicrotome with a diamond knife. The samples were examined at an accelerating voltage of 120 k. The TEM images were obtained using Soft Imagine System software.

4. Results and discussion

4.1. FT-IR spectroscopic analysis

Fourier transform infrared spectroscopy (FT-IR) analysis has been widely used to identify the interaction and the phase behavior