



Transparent bionanocomposites with improved properties from poly(propylene carbonate) (PPC) and cellulose nanowhiskers (CNWs)



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ABSTRACT

Bionanocomposites of poly(propylene carbonate) (PPC) reinforced with cellulose nanowhiskers (CNWs) were prepared through simple solution technique. The obtained PPC/CNW films containing CNWs in the range of 1–10 wt% were highly transparent in the visible region. The morphology, mechanical properties, and thermal properties of the nanocomposites were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), static and dynamic mechanical measurements, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results showed that CNWs were uniformly dispersed in PPC matrix and the incorporation of CNWs significantly increased the tensile strength and storage modulus of PPC. More interestingly, the elongation at break of PPC/CNW nanocomposite films remained as high as above 900%. In addition, CNWs also increased the thermal stability and vicat softening temperature (VST) of PPC. This work provides a good example for preparation of biopolymer nanocomposites with improved properties by the incorporation of CNWs.

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1. Introduction

In the last century, various synthetic polymers, most of which originate from non-renewable fossil fuels, have been rapidly developed as the most widely used materials [1]. However, the preparation of the synthetic polymers not only consumes large quantities of petroleum resources, but also causes serious “white pollution”. It is urgent to use biodegradable packing materials, especially for short-term packaging and disposable applications. During the past two decades, intense efforts have been made to develop biodegradable natural polymers (such as cellulose, starch and protein) and synthesized polymers (such as polylactic acid (PLA), polycaprolactone (PCL), and poly- β -hydroxybutyrate (PHB)) from renewable sources are explored as alternatives to non-biodegradable polymers [2].

Poly(propylene carbonate) (PPC) is a kind of new biodegradable polymer that is synthesized by copolymerization of propylene oxide and carbon dioxide. PPC has attracted increasing interest in both research and industry due to that the synthesis process of PPC could reduce the emission of greenhouse gas and save precious fossil-based raw materials. Moreover, PPC has potential applications in packaging field owing to its excellent barrier properties, good ductility and low cost [3]. However, its poor thermal stability and relatively low mechanical strength seriously limit its practical applications. Therefore, improving the thermal and mechanical

properties of PPC through chemical modification of PPC chains [4], and physical blending with other polymers [5–8] or inorganic fillers is of great significance [9–16]. Unfortunately, the high transparency and good toughness, which are inherent advantages of PPC, were lost in the final PPC blends and composites in the most previous studies [13,16].

Cellulose nanowhiskers (CNWs), extracted from natural cellulose such as cotton, wood and tunicate by acid hydrolysis, are fibers with nanoscale diameter. CNWs not only presents cellulose advantages such as renewability, biodegradability, nontoxicity, but also possesses other outstanding properties, including high specific strength, high crystallinity and stiffness, making them attractive nano-fillers for polymers [17–22]. However, the hydrophilic nature of CNWs makes them difficult to uniformly disperse in common nonpolar solvents or in hydrophobic matrix and thus an aggregation of CNWs often occurs. In addition, agglomeratetion of CNWs as a result of strong hydrogen bonds occurs upon drying that is hard to be re-dispersed even under prolonged sonication [23–25]. To improve the dispersibility of CNWs in a polymer matrix, chemical modification and surfactant addition are the most used practices [20,26–29]. But the chemical modification would often destroy the crystalline structure of CNWs, and then ultimately decrease their stiffness [26]. Further, higher amount of surfactants is needed for the high surface area of CNWs [27]. More recently, template method based on solvent exchange is also developed to prepare polymer/CNW nanocomposites [30,31]. However, this process is complicated and time consuming since the CNWs have to retain in aqueous medium before solvent exchange process.

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Recently, re-dispersible CNW powder was successfully prepared in our laboratory, and the obtained CNW can be easily dispersed in kinds of solvent [32]. In the present work, to develop biodegradable plastic to tackle sustainability challenges, we report here the preparation of bionanocomposites based on PPC and CNW via a simple solution mixing method. The nanoscale CNWs were found to be uniformly dispersed in PPC matrix and the mechanical properties and thermal stability of PPC are significantly improved. Meanwhile, the nanocomposites retained the inherent high transparency and good elongation of PPC.

2. Experimental

2.1. Materials and characterization

The PPC was purchased from Tianguan Enterprise Group Co. Ltd. (Henan, China, Mn: 70K, PDI: 2.13). The removal of catalyst in PPC was performed with aqueous hydrochloric acid followed by an additional neutralization and water wash. To remove the polyether-containing chains, cyclic products, solvents and excess epoxides, the purified PPC was precipitated from an organic solution with a large excess of ethanol [32]. The re-dispersible solid CNW was prepared in our laboratory [33]. N-methyl-2-pyrrolidone (NMP) was analytical reagent and used as received.

The TEM images were recorded on a transmission electron microscope (JEOL 2200 FS) with acceleration voltage of 200 kV. The samples for TEM analysis were prepared by microtoming 50–100 nm thickness films from the nanocomposites with an ultramicrotome (UC6&FC6, Leica) at -60°C .

The morphology of the brittle fractured surface of the composite films was observed with a scanning electron microscope (JEOL 6700 F) at 5 kV and 10 A. The fractured surface was put on a conducting carbon tape stuck on the stub and coated with Pt.

The optical spectrum of the film was recorded on a UV-vis spectrophotometer (PERSEE TU-1901) in the wavelength range from 400 to 800 nm.

Dynamic mechanical analysis (DMA) was performed using a dynamic mechanical analyzer (DMA Q800, TA instrument). The data was recorded from -20 to 80°C at a heating rate of $3^{\circ}\text{C}/\text{min}$ and a frequency of 1 Hz. The glass transition temperature was obtained from the maximum of $\tan \delta$.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 instrument under a nitrogen atmosphere. For every test, the samples were heated at a rate of $20^{\circ}\text{C}/\text{min}$ from -30 to 70°C , then quenched to -30°C and finally heated again to 70°C at a rate of $20^{\circ}\text{C}/\text{min}$. The T_g was gotten from the second heating run to minimize the thermal history effect.

Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer Pyris1 instrument from 40 to 600°C at a heating rate of $20^{\circ}\text{C}/\text{min}$ in a dry nitrogen environment.

Tensile testing of neat PPC and PPC/CNW composites was performed using an Instron testing machine (Instron 3365) at 23°C with a crosshead speed of 100 mm/min. The rectangular tensile specimens were cut with a length of 70 mm and a width of 5 mm. In order to ensure accuracy and repeatability, at least 7 specimens were tested.

The vicat softening temperature (VST) of the composites was determined according to ASTM D 1525 using the VST tester (XRW-300, Chengde Jinjian Testing Instrument Co., Ltd., China).

2.2. Preparation of PPC/CNW composites

The PPC/CNW nanocomposites were prepared by solution casting. First, certain amount of CNWs was dispersed in NMP by sonicating for 10 min to get transparent CNW/NMP suspension. After

then, required amount of PPC was added to the above suspension and dissolved by continuously stirring at room temperature for 3 h, then sonicated for another 3 min to ensure the uniform dispersion of CNWs. The concentration of PPC in NMP was about 8 wt%. The mixed solution was cast on glass plate, and dried at 60°C . After the solvent was completely evaporated, the PPC/CNW composite films with the thickness of about $30\ \mu\text{m}$ were obtained. Using the same procedure, a series of PPC/CNW nanocomposite films containing 0, 1, 3, 5, 7, and 10 wt% CNW were prepared. For the characterization of vicat softening temperature, a part of solution was precipitated with ethanol and dried in vacuum at 60°C and the dried samples were injection molded into specimens with dimensions of $10 \times 10 \times 4\ \text{mm}$ employing a HAAKE MicroInjector Instrument.

3. Results and discussion

3.1. Morphology

As a new kind of nanoscale fiber-like filler, CNW is well known for its high rigidity to reinforce polymer matrix, without sacrificing the transparency of polymers [34–37]. Fig. 1 shows the photographs of neat PPC (a) and PPC/CNW (10 wt%) nanocomposite (b) films. It can be seen that, even with the CNW content of 10 wt%, the nanocomposite was still quite transparent compared to unfilled PPC. The transparency of PPC and PPC/CNW nanocomposite films was further characterized by measuring the light transmittance in the wavelength from 400 to 800 nm using a UV-vis spectrophotometer, and the spectra are shown in Fig. 2. The films of neat PPC and PPC/CNW nanocomposites with the CNW contents from 1 to 10 wt% had similar transmittance as high as above 80%. The transparency of the nanocomposites was maintained with only a small decrease of the light transmittance compared with pure PPC. The good transparency was ascribed to the dimension of CNW smaller than the wavelength of visible rays [38]. Besides that, we suggest that the CNWs in the PPC matrix had well dispersion and formed network structure, so that the PPC/CNW nanocomposites was free from light scattering.

To evaluate the dispersion of the CNW in PPC, SEM observations for the fracture surface of PPC/CNW nanocomposite films were carried out and the fractographs are shown in Fig. 3. When the CNW content was below 5 wt%, the fracture surfaces of nanocomposites exhibited some wrinkled structure, indicating the ductile fracture characteristics. When the CNW content was 7 wt% and 10 wt%, many tiny white dots appeared on the fracture surface of nanocomposites which might be attributed to the transversal section of CNWs [23]. These tiny white dots appear to be well embedded in the matrix, suggesting a rather good dispersion of CNWs in the PPC matrix and strong intersurface interaction between CNWs and PPC. At the same time, the appearance of white dots indicated the CNW network structure formed in PPC matrix. In all the SEM observations, there was no evidence of micrometerscale agglomerates of CNWs. The well dispersion and the network structure formation of CNW were significant to the transparency and mechanical properties of polymer/CNW nanocomposites.

The dispersion of CNW in PPC matrix was further characterized by TEM. In the three graphs of Fig. 4, CNWs were dispersed well in PPC matrix. However, the low contrast between PPC and CNW made the TEM image was not very clear. At 1 wt% content, pointed by white arrows, CNWs were found to be uniformly and randomly dispersed in PPC matrix. The randomly dispersion of CNW means that in the process of solvent evaporation and film formation, there was no preferred orientation conducted on CNW. When the CNW content reached 5 wt%, CNWs were still well dispersed, and a very obvious network structure was formed. Similar network structure

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