Carbohydrate Polymers 142 (2016) 206–212

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Modification of cellulose nanocrystal via SI-ATRP of styrene and the mechanism of its reinforcement of polymethylmethacrylate

Y. Yin, X. Tian, X. Jiang*, H. Wang, W. Gao

Key Laboratory of Eco-textiles of Ministry of Education, College of Textiles and Clothing, Jiangnan University, Wuxi 214122, Jiangsu, China

ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form
21 December 2015
Accepted 10 January 2016
Available online 12 January 2016

Keywords:
Cellulose nanocrystals
Polystyrene
Surface-initiated atom transfer radical polymerization
Polymethylmethacrylate

ABSTRACT

Cellulose nanocrystal (CNC) is a promising strengthener but is used limitedly since its poor compatibility with organic materials. The graft polymerization of styrene via surface-initiated atom transfer radical polymerization (SI-ATRP) of cellulose nanocrystal is adopted to modify its thermo-stability and compatibility. The modified crystals have been dosed into polymethylmethacrylate (PMMA) nanocomposites by the solution casting. The polymeric layer on the surface of CNCs should improve the thermal stability of CNCs, and provide significant dispersibility and compatibilization for the nanocomposites. Thermogravimetry analysis proved that the initial degrade temperature of CNC was increased 50 °C with the modification. The scanning electronic microscope showed that the modified CNCs homogeneously dispersed in PMMA matrix. Breaking strength and elongation at break of the composites were improved, which was attributed to the reinforcement of CNCs modified with styrene. Transmittance of nanocomposite films measurement showed that the transmittance of PMMA/1%CNC was almost close to that of pure PMMA.

1. Introduction

Cellulose, which is one of the most abundant natural polymers, is a promising renewable, biodegradable raw material with an excellent low cost (Brinchi, Cotana, Fortunati, & Kenny, 2013; Lima & Borsali, 2004; Frone, Berlioz, Chailan, & Panaitescu, 2013). Cellulose and its derivate have been used extensively to reduce the petroleum-dependent materials and the environment pollution accordingly. To the best of our knowledge, the most valuable material of cellulose is cellulose nanocrystal (CNC), which has attracted much interest in the field of materials (Peresin, Habibi, Zoppe, Pawlak, & Rojas, 2010; Yang, Han, Duan, Xu, & Sun, 2013; Lee, Aitomaki, Berglund, Oksman, & Bismarck, 2014). With large specific surface area and excellent mechanical properties, a recyclable material, namely CNC is studied extensively in recent decades (Habibi, Lucia, & Rojas, 2010). CNC has a strength over 10 GPa and a modules over 150 GPa, which is as large as graphene (Lin, Huang, & Dufresne, 2012). The specific strength of CNC is about 85 $J g^{-1}$, which is over three times of steel (25 $J g^{-1}$) (Nishino, Takano, & Nakamae, 1995). To develop a reinforced Nano composite is considered as the most prospective utilization of CNC (Pei, Malho, Ruokolainen, Zhou, & Berglund, 2011).

The preparation, stability and compatibility are the key problems of the utilization of CNCs. The preparation based on sulfuric acid hydrolysis has been the most common method since it was found by Rånby (1949), Rånby and Ribi (1950). The resulted CNCs present inferior thermal stability, on account of the sulfate groups from the sulfuric hydrolysis (Lin & Dufresne, 2013). In addition, CNCs tend to agglomerating irreversibly in the process of drying because of the formation of inter- and intra-molecule hydrogen bonds. Furthermore, the regular structure and hydrophilicity of the cellulose make it incompatible to the nonpolar materials. There are thus two disadvantages of CNC while utilized in reinforcement of organic polymer material, one is the low inferior thermal stability, and the other is the poor compatibility to the nonpolar materials.

Surface modification is proved to be an efficient method for overcoming the two problems mentioned above. Many processes of surface modification have been studied, such as adsorption of surfactants (Heux, Chauve, & Bonini, 2000; Bondeson & Oksman, 2007; Kim et al., 2009; Rojas, Montero, & Habibi, 2009). TEMPO-mediated oxidation (Habibi, Chanzy, & Vignon, 2006; Batmaz et al., 2014; Montanari, Roumani, Heux, & Vignon, 2005), cationization (Montanari et al., 2005), esterification (Mariano, Kissi, & Dufresne, 2014; Sobkowicz, Braun, & Dorgan, 2009) and polymer grafting (Ljungberg et al., 2005; Kan, Li, Wijesekera, & Cranston, 2013; Mangalam, Simonsen, & Benight, 2009; Habibi & Dufresne, 2008). The previous studies are good attempts. However, the weak combination of the modifier and cellulose in surface absorption results

---

* Corresponding author. Tel.: +86 510 8591 2007; fax: +86 510 8591 2009.
E-mail address: jiangx@jiangnan.edu.cn (X. Jiang).

http://dx.doi.org/10.1016/j.carbpol.2016.01.014
0144-8617/

in a low durability, as well as the weak compatibility of the modifier and cellulose in organic reaction causes a low efficiency of modification. These disadvantages can be avoided by the graft polymerization, but the limited controllability of the traditional radical polymerization leads to poor control of the structure of the grafted molecular chain. UV radiation (Adeel et al., 2014; Bhatti, Adeel, Siddique, & Abbas, 2014a) and gamma radiation (Adeel et al., 2015; Gulzar et al., 2015; Ajmal et al., 2014; Bhatti, Adeel, & Taj, 2014b; Khan et al., 2014) were utilized in the modification of cotton fabric or powder. These methods are becoming popular because of their high treatment speed, easy to use and cost effectiveness. However, the problem of poor control of the structure of the grafted molecular chains still existed. Therefore, a controlled polymerization should be the best alternative modification of CNC (Zoppe et al., 2010; Majoinen et al., 2011; Lacerda, Barros-Timmons, Freire, Silvestre, & Neto, 2013; Morandi, Heath, & Thielemans, 2009). The studies about the modification of the CNC with controlled polymerization should be preceded intensively.

Surface-initiated atom transfer radical polymerization (SI-ATRP) of styrene, the mechanism of which has been studied by Morandi et al. (2009), was employed in the current study to modify the surface of CNC. The structure of the modified CNC was characterized. The CNC grafted with polystyrene chains were then mixed with poly (methyl methacrylate)(PMMA) as a reinforcing bionanofiller, to prepare PMMA nanocomposites. The thermal and mechanical properties of the materials were studied, and the possible mechanism of the reinforcement was also discussed.

2. Experimental

2.1. Materials

Sulfuric acid, microcrystalline cellulose (MCC), triethylamine, *N*,*N*-dimethylformamide (DMF), dichloromethane, ethanol, copper(I) bromide, anisole, styrene and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Limited Company (SCRC); 2-Bromoisobutyryl bromide, 2-bromoisobutyrate, *N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine (PMDETA) and PMMA were obtained from J&K Scientific Limited Company. The styrene was distilled over 2,5-di-*tert*-butylhydroquinone under vacuum and stored at 4 °C. The others are used without further treatment.

2.2. Sulfuric acid hydrolysis

About 10 g of MCC were mixed with 200 mL sulfuric acid aqueous solution (64 wt.%) in a three-neck flask, which were set with stirrer, thermometer and condenser, respectively. The reactive mixture was kept stirring for 1 h at 45 °C for hydrolysis, then about 200 mL of cold water (about 0 °C)was poured into the obtained suspension to stop the reaction. Subsequently, the suspension was centrifuged at 10,000 rpm till it had no obvious stratification and existed as a kind of transparent dispersion. After that, dialysis against distilled and deionized water was kept going for several days till the pH of the water reached a value of 7.0, in order to remove the remained free acid in the dispersion. Finally, cellulose nanocrystal (CNC) was received after freeze-drying.

2.3. Surface grafting reaction

Macromolecular initiator was prepared from the reaction between 2-Bromoisobutyryl bromide (Br-iBuBr) and CNC with the catalysis of triethylamine. About 26 mL of Br-iBuBr was added into the mixture containing CNC, triethylamine and DMF, and the mixture was kept stirring at 70 °C for 24 h under the protection of a nitrogen. The reacted mixture was filtered through a Buchner funnel and the crude product was received. Finally, the crude product was purified by way of Soxhlet extractions with dichloromethane (24 h) and ethanol (24 h), and the esterified CNC, namely macroinitiator was prepared.

About 50 mL of anisole, 50 mL of styrene and 0.7 mL of 2-bromoisobutyrate were introduced into the mixture of copper(I) bromide loaded in three-neck flask. Followed by adding appropriate PMDETA. The reaction was performed at 100 °C for 12 h under nitrogen atmosphere. The grafted NCCs were obtained by filtration through a Buchner funnel and purified by Soxhlet extractions with dichloromethane (24 h) and ethanol (24 h). The remaining polystyrene homopolymer was removed by washing against methanol by centrifugation.

2.4. Characterization

Transmission electron microscopy (TEM) was performed on a JEM-2100 electron microscope operation at an acceleration voltage of 200 kV to characterize the morphology and distribution of cellulose nanocrystals. Infrared spectra was recorded at room temperature on NICOLET is 10 Fourier transform infrared spectroscopy (FT-IR) to characterize the surface modification of CNCs. The samples were prepared by KBr pellet method. The resolution of the spectrometer is 4 cm^{-1}, the wave number range is 400–4000 cm^{-1}, and the samples were scanned 30 times. The chemical structure of CNCs modified with styrene was characterized with Bruker 400 M solid-state ^{13}C NMR. Thermostability of CNCs and PMMA composites was analyzed by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). The thermal degradation of CNCs and composites was analyzed using thermal analyzer TGA/SDTA851e under nitrogen flow. The samples were heated from 30 to 550 °C at a heating rate of 10 °C min^{-1}. The glass transition temperature of PMMA composites was measured with a Pyris 1 DSC instrument. The samples were scanned from 30 to 200 °C at a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) patterns of raw MCC, manufactured CNCs and modified CNCs was recorded on Bruker Siemens D8 X-ray diffractometer operated at 3 kW with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) in the range $2\theta = 3$–60° with a step of 0.02°. The homogeneity of PMMA composites was observed using scanning electron microscopy (SEM) su1510 device (Hitachi Zosen Corporation) at 30 kV. The mechanical properties of Nano composites were investigated through breaking strength and elongation at break. UV–vis spectrophotometer was utilized at wavelength from 400 to 800 nm to measure the transmittance of nanocomposite films.

3. Results and discussion

Transmission electron microscope (TEM) was employed to get the information of the morphology and average size of the cellulose nanocrystals (CNCs), which was shown in Fig. 1. Wherein, Fig. 1A and C were TEM photos of the obtained pure CNC and CNC modified with PSt, while Fig. 1B and D were the static size distributions of the length of the pure CNC and CNC modified with PSt. Perfect long bony fiber-like morphology of CNC could be observed in Fig. 1A. It suggested that the separation of the fiber through hydrolysis was successful. The size of CNC was calculated statically, as shown in Fig. 1B. One hundred nanofibers were selected and measured with the ruler tool. The result showed that the average length of CNC was about 120–180 nm. As shown in Fig. 1C and D, the length of CNC modified with PSt was not apparently changed. However, the diameter of the modified CNC was decreased. These results revealed that the morphology of CNC modified with PSt was not apparently destroyed.