Carbohydrate Polymers 125 (2015) 352–359

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Preparing cellulose nanocrystal/acrylonitrile-butadiene-styrene nanocomposites using the master-batch method

Libo Ma[a,b,c], Yang Zhang[a], Yujie Meng[c], Phuriwat Anusonti-Inthra[d], Siqun Wang[c,*]

[a] College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China
[b] Department of Materials Engineering, Changzhou Institute of Engineering Technology, Changzhou 213164, China
[c] Center for Renewable Carbon, University of Tennessee, Knoxville, TN 37996, USA
[d] Space Institute, University of Tennessee, Tullahoma, TN 37388, USA

ARTICLE INFO

Article history:
Received 2 October 2014
Received in revised form 12 February 2015
Accepted 26 February 2015
Available online 6 March 2015

Keywords:
Cellulose nanocrystal
ABS
Master-batch
Composites
Extrusion

ABSTRACT

The master-batch method provides a simple way to apply cellulose nanocrystal (CNC) as reinforcement in a hydrophobic matrix. The two-stage process includes making high-CNC content (70 wt%) master batch pellets, then mixing acrylonitrile-butadiene-styrene (ABS) and maleic anhydride grafted polyethylene with the master batch pellets to prepare the ABS/CNC nanocomposite in extruder. SEM image indicates that self-assembled CNC nanosheets disperse evenly throughout the polymer matrix. The improved mechanical properties shown in tensile and DMA tests reveal that the CNC combines well with the ABS. TGA results show that the thermal degradation temperature of CNC in the master batch increases because of the protection of the ABS coating. This approach not only improves the dispersion ability and the thermal stability of CNC, but it is also applicable to use with other hydrophobic thermoplastics in industrial scale production.

1. Introduction

As awareness of the importance of protecting the environment grows, methods of getting products from renewable, sustainable, biodegradable, non-petroleum-based, and environmentally friendly resources are being widely studied. One such resource is natural cellulose, which exists in almost every green plant; cellulose gives plants high-quality mechanical properties that are widely applicable to many uses. For example, we use wood products as engineering materials in construction, and to produce paper, textiles, etc. In addition, natural cellulose can also be used as reinforcement in the composites industry (Cheng, Wang, Rials, & Lee, 2007; Lee & Wang, 2006; Lee, Wang, Pharr, & Xu, 2007).

However, modern industry demands very high-performance cellulose materials if they are to be used in automobiles, electronics, medical applications, aerospace, and so on. In recent years, nanotechnology has attracted much attention from researchers because materials on the nanoscale can exhibit many intriguing properties. One important material is cellulose nanocrystal (CNC), 5–20 nm wide, 100–500 nm in length, with an aspect ratio of (10–70), which can be isolated from such sources as wood, cotton, bamboo, grass, tunicates, bacteria, and more. The theoretically predicted elastic modulus and tensile strength of CNC are close to 150 GPa and 10 GPa, respectively (Sakurada, Nukushina, & Ito, 1962).

CNC is recyclable and has excellent mechanical properties. The technology of isolating nanocellulose from natural resources has been mastered by many researchers (Frone et al., 2011; Wang & Cheng, 2009). Nevertheless, how to put nanocellulose to good use in industry is still being studied (Biyani, Foster, & Weder, 2013; Cheng, Wang, & Rials, 2009).

Polymers reinforced by CNC have not been widely used on an industrial scale because (1) CNC are polar and hydrophilic, so they are not compatible with non-polar and hydrophobic polymers; the compatibility between CNC and polymers is not good; (2) dispersing CNC into polymers evenly without any treatment is difficult because there are many hydroxyl groups; these make CNC easily form hydrogen bonds, which in turn cause agglomeration and reduce the efficiency of the mechanical reinforcement (Eichhorn, 2011); (3) CNCs will thermally degrade when the processing temperature is above 200 °C, restricting their application in many polymers whose processing temperatures are relatively high (most are over 200 °C), such as the major engineering plastics PA, PC, PET, PPO, etc.

When CNC-reinforced hydrophobic polymers are being produced, the solution casting method is chosen in most cases to avoid the drawbacks of the CNC. In brief, the polymer matrix must be dissolved into the solvent first, and nanocellulose is introduced into this phase to form an even solution; the mixture is then cast to

* Corresponding author. Tel.: +1 865 946 1120; fax: +1 865 946 1109.
E-mail address: swang@utk.edu (S. Wang).

http://dx.doi.org/10.1016/j.carbpol.2015.02.062
0144-8617/

form films after the solution dries out (Bahar et al., 2012; Fujisawa, Ikeuchi, Takeuchi, Saito, & Isogai, 2012; Liu, Liu, Yao, & Wu, 2010; Siqueira, Bras, & Dufresne, 2009; Svagan, Azizi Samir, & Berglund, 2007).

However, the inefficiency of the solution casting limits CNC use on the industrial scale. Instead, melt-blending methods such as extrusion molding and injection molding have been widely used in the thermoplastic processing industry. In recent years, the potential of thermoplastic/CNC nanocomposites using the melt-blending method has attracted extensive research, such as PS (Lin & Dufresne, 2013), PA11 (Panaitescu, Frone, & Nicolae, 2013), and PA6 (Corrêa et al., 2014). In studies of LDPE/CNC composites, when CNCs were coated with poly (ethylene oxide) and were then melt-blended with LDPE, the dispersibility and thermal stability of the CNCs were improved (Ben Azouz, Ramires, Van den Fonteyne, El Kissi, & Dufresne, 2011; Pereda, El Kissi, & Dufresne, 2014).

The master-batch method is widely used in the polymer processing industry. Usually there are at least three components in the master batch: (1) the functional fillers, which are the main body of the master batch; (2) the matrix, which, as the carrier, is usually composed of polymers; (3) the dispersing agent, which can improve the dispersibility of fillers in the objective polymers. Gong, Pyo, Mathew, and Oksman (2011), using this method, prepared PVA/CNF composites and found that the tensile properties were improved. Arrieta et al. (2014) prepared a PLA-PHB master batch first, and then mixed it with CNC to prepare nanocomposite films. Both the dispersibility of the CNC and the processability of the composites were improved.

Acrylonitrile-butadiene-styrene (ABS) is an engineering polymer widely used for its relatively low cost and good mechanical properties. ABS has superior dimensional stability and can be easily processed into products with exact dimensions and excellent surface appearance compared to polyolefin plastics. It can be produced for structural components in automobile, enclosures of electrical and electronic parts, and home appliances, as well as other industrial parts (Shin et al., 2010). However, CNC-reinforced ABS nanocomposites have not been reported in the literature, possibly due to CNCs' limitations.

In this study, we first prepared a high CNC-content master batch through the master-batch method to improve the dispersibility, the thermal stability, and the compatibility between the CNC and the matrix. The CNC master-batch was then used to produce the ABS/CNC nanocomposites via melt extrusion. The goal of this work was to put forward one way to use CNC on an industrial scale with good operability and cost effectiveness.

2. Materials and methods

2.1. Materials

Cellulose nanocrystal (CNC) in water suspension was purchased (University of Maine, USA), with a solid content of 6.5 wt%. Acrylonitrile-butadiene-styrene (ABS) was purchased in China (Ningbo Taihua, AG15A1); maleic anhydride grafted polyethylene (MAPE) was purchased from Parkson New Material Co. (HAD-14A, with a melting point of 135 °C and a grafting rate of 1.8%, China). Paraffin emulsion (Cascowax EW-58LV) was purchased from Momentive Specialty Chemicals Inc., USA. Acetone was acquired from Klean-Strip (1-gal, Model # GAC18, USA).

2.2. Master-batch method for preparing high-CNC content pellets

First, the ABS was dried at 60 °C for 6 h in a vacuum oven to reduce the moisture content to less than 1 wt%, and then it was dissolved into acetone at ambient temperature by magnetic stirring for 24 h. The ABS content in the acetone solution was 15 wt%.

A CNC water suspension with 6.5 wt% concentration was poured into a metal container and sealed. Samples were then placed into liquid nitrogen for 5 min for rapid freezing, followed by freeze-drying in a vacuum lyophilizer (Labconco, Inc., Kansas City, MO) at a temperature of -51 °C for three days. An ultra-light sponge-like aerogel was obtained. The lyophilizates were oven-heated at 40 °C for 6 h to remove surplus water. The dried CNC was then put into a kitchen blender and acetone was added; at this point, the CNC content was 5 wt%. The blending time was 5 min. Then the solution was treated for 20 min with high intensity ultrasonication (HIUS) (Cheng et al., 2009) (Sonic Newtown, CT, 20 kHz, Model 1500 W) to isolate the freeze-dried CNC. After the CNC/acetone and ABS/acetone solutions were mixed together, paraffin emulsion was dropped into the mixed solution as the dispersing agent. The weight ratio of ABS, CNC, and paraffin was 29:70:1. The mixed solution was magnetically stirred under the chemical hood to cause the acetone to evaporate. In the end, solid pellets with a high content of CNC (70 wt%) were obtained, which were kept as a master batch for future use.

2.3. Preparation of ABS/CNC nanocomposites via melt extrusion

The ABS-and-CNC master batch was oven-heated at 60 °C for 6 h to reduce the moisture content to less than 1 wt%. The CNC master batches, the ABS and the MAPE were then melt blended by means of a two-screw extruder (MinLab Rheomex CTW5, Thermo Haake). The melt extruding temperature was 180 °C, the screw speed was set at 100 RPM, and the mixture was mixed in the extruder for 5 min before being squeezed out. The resulting composites were denoted as ABS/CNC0.7, ABS/CNC0.7M, ABS/CNC2.1M, ABS/CNC3.5M, and ABS/CNC7M. The numbers represent the wt% content of CNC in the composites, and the letter "M" signifies that MAPE 1 wt% was added to the composites. Meanwhile, ABS/CNC7MD was prepared. Between ABS/CNC7M and ABS/CNC7MD, the only difference was that the freeze-dried CNC was added directly ("D") into the matrix at the melt blending stage.

The extrudates were dried for 24 h in a vacuum oven at 60 °C then compression-molded through the compressing machine (CARVER, 3895.4PR1A00, USA) at a temperature of 180 °C; they were preheated for 5 min (6 bar) and 3 min under pressure (100 bar) and then cooled to a temperature of 50 °C. After compression-molding, ABS/CNC nanocomposite sheets with different CNC contents were obtained.

2.4. Characterization

2.4.1. Microscopy examination

The morphologies of the freeze-dried CNC and ABS/CNC nanocomposites were investigated using a SEM (Zeiss Auriga SEM/FIB crossbeam workstation). The inner structures of the freeze-dried CNC, the CNC master batch, and the fractured surfaces of the ABS/CNC nanocomposites after tensile testing were compared.

2.4.2. Tensile tests

The modulus and tensile testing were measured using a universal testing machine (Model 5567, Instron, Inc., Canton, MA) in accordance with ASTM D638. Dumbbell-shaped tensile bars were punched from the ABS/CNC nanocomposite sheets. Before the measurements, all the samples were conditioned for 24 h. All samples were tested at 23 ± 2 °C and 50 ± 5% relative humidity. Each type of treatment was replicated 10 times at a crosshead speed of 1 mm/min.