Green Nanocomposites Reinforced with Cellulosic Crystals Isolated from Juvenile Poplar

Qingzheng Cheng*
*Corresponding author
q.cheng@mail.wvu.edu
Jingxin Wang
jxwang@wvu.edu
Division of Forestry and Natural Recourses
West Virginia University
Morgantown, WV, USA

Abstract

Green nanocomposites are expected as the next generation of materials for the future, opening up opportunity to replace conventional petroleum-based composites as a new, biodegradable, high performance, lightweight green material. In this study, cellulosic nanofibers (CNFs) were isolated from a juvenile poplar (P. trichocarpa) (PT) and a juvenile hybrid poplar (HP) using acid hydrolysis. Film casting method was used to fabricate biodegradable nanocomposites from CNF and poly(vinyl alcohol) (PVA) solution. CNFs were characterized using atomic force microscopy and dynamic light scattering. Most of nanofibers were bundles of single nanocrystals and the average diameter of the nanofibers was about 21 nm. The mechanical properties and thermal degradation behavior of the nanocomposites were analyzed by tensile test and thermogravimetric analysis, respectively. The elastic modulus of PVA was significantly improved by the CNFs, while the strength of the composites was comparable with that of pure PVA. No significant differences of tensile mechanical properties of PVA nanocomposites reinforced with CNFs isolated from PT and HP were detected. The thermal degradation behavior of PVA was improved by CNFs.

Keywords: Cellulose, Isolation, Nanocomposites, Nanofiber, Properties, Reinforcements
Introduction

Bio-based nanocomposites are considered one of the green materials for the next generation. The market for these bio-based nanocomposites has the potential for dramatic growth with a green concept in recent years. The bio-based nanocomposites can be produced from renewable resource-based polymers in combination with nano-filler reinforcement, such as cellulose nanocrystals and nanofibers, for a variety of applications. Nanocomposites of this category are expected to possess improved strength and stiffness with small reduction in toughness, reduced gas/water vapor permeability, a lower coefficient of thermal expansion, and an increased heat deflection temperature (Ray and Okamoto 2003, Samir et al. 2004, Zimmermann et al. 2004). Bio-based nanocomposites have the greatest market growth potential in industries, where biocompatibility and environmentally responsible design and constructions are required. The potential applications include biomedical tissue, car interiors, packaging materials, electronics, and housing appliances.

The research on nanocomposites reinforced by cellulose fibrils/crystals has grown very fast because of its environmentally friendly features and the improvement of stiffness and strength in recent years (Samir et al. 2004, Zimmermann et al. 2004). In this study, we used a hybrid poplar and its grandmother samples as raw materials to isolate nanofibers and nanocrystals and to fabricate cellulosic nanocomposites. Many terms have been used to describe different types of cellulose fibrils, such as microfibrillated cellulose (MFC), cellulose nanocrystal, cellulose nanofibril, cellulose whisker, cellulose nanofibers. Cellulosic nanofibers were used in this paper.

Poplar trees are suitable candidates for genetic improvement for biofuels and bioproducts production due to their modest genome size, fast growth, amenability to genetic engineering and vegetative propagation, and adaptability to a wide range of planting conditions. The hybrid poplar plantation (Populus trichocarpa x Populus deltoides) was established from vegetative cuttings at the West Virginia University Agronomy Farm. In order to examine the potential of hybrid poplar and its parents’ tree clones for polymer reinforcement to fabricate cellulosic bio-nanocomposites, a child and its grandmother samples were used in this study.

Materials and Methods

Materials

Two poplar samples, black cottonwood (Populus trichocarpa) (PT) and hybrid poplar (HP), were used as raw materials for nanofiber isolation. Microcrystalline cellulose (MCC, Avicel PH-101, supplied by FMC BioPolymer) was used as reference material. Poly(vinyl) alcohol (PVA) (99-100% hydrolyzed, Acros) was used as composite matrix. Sulfuric acid (H₂SO₄, SA170-4, 70% Textile) was purchased from Acros. Sodium chlorite (NaClO₂, unstabilized, tech., 80%), sodium hydroxide (NaOH), and acetic acid solution (1N) were purchased from Fisher Scientific.
Cellulosic nanofiber isolation and characterization

The poplar samples were debarked, dried, and milled to particles passing a 60-mesh screen. The lignin in wood particles was removed using acidified sodium chlorite solution (Abe 2007, Wise 1946). The lignin removed samples were then placed in a 60% H₂SO₄ (v/v) solution for 2 h at 45°C with medium stirring. The cellulose to acid ratio was 1:10 g/mL. After hydrolysis, the mixture was centrifuged and decanted. A solution of 2% sodium hydroxide was added to the centrifuge solids to neutralize any remaining acid and the centrifugation repeated several times. Then deionized water was added to the centrifuge solids to rinse for 2-3 times. The solid particles were subjected to ultrasonic irradiation in deionized water for 3 min at 50% power to disperse the nanofibers (Choi and Simonsen 2006). An atomic force microscopy (AFM) (Veeco Metrology) with non-contact mode after a small drop of fibril suspension was dried on a mica sheet to characterize the morphology of the nanofibers. And a dynamic light scattering (DLS) (Agilent 7030 Nicomp) were used to measure the diameter distributions of the cellulosic nanofibers.

Nanocomposites preparation and characterization

PVA water solution (10 wt%) and cellulose nanofiber water suspension or MCC were mixed and stirred manually and then dispersed by ultrasonic treatment for about one minute with 50% power level. The film casting method was used to make nanocomposite film in propylene dishes (Cheng et al. 2007, Cheng et al. 2009b). The samples were kept in a desiccator before the mechanical properties were characterized. The composites with three levels of fibril loading (1%, 2%, and 5%) were manufactured and tested. The nominal thickness of the composites was 150 μm.

The mechanical tests were performed using an Instron testing machine (Model 5869). The crosshead speed was 2.5 mm/min. Crosshead extensions were used as the specimen deformations to calculate the tensile strain. The samples were cut to dogbone shapes with width of 5 mm for the narrow portion and total length of 40 mm (gauge length was 20 mm). Based on ASTM D1708 standard (ASTM 202), five specimens were tested for each composition. Single parameter test of analysis of variance (ANOVA) was used to examine the influence significance of the cellulose contents on tensile properties of the composites (α=0.05). The thermal degradation behavior of the composites was conducted by a thermogravimetric analyzer (TGA Q50, TA Instruments). The temperature range was from room to 400 °C. Heating rate was 20 °C/min. Nitrogen gas rate was 20 ml/min to avoid oxidation. The sample weights were between 2-3 mg. TA Instruments Software was used to transform the TG curve to the derivative thermogravimetric (DTG) curve. The combination of TG and DTG thermograms gives a clear indication of number of stages of the thermal degradation (Renneckar et al. 2004).
Results and discussion

Characterization of wood particles and nanofibers

The wood particles were changed to white after lignin was removed. The microstructure of wood particles was irregular and most particles were smaller than 200 µm. After acid hydrolysis, there were still some big particles with length more than 100 µm and a turbid suspension presented for all samples, but after ultrasonic treatment, the suspensions were transparent. The average diameter of the nanofibers was about 21 nm measured by dynamic light scattering (Fig. 1), which indicated that the nanofiber were still bundles of single nanocrystals because a single wood cellulose crystal is about 3-5 nm in diameter (Beck-Candanedo et al. 2005). The AFM height images were further illustrated that the diameters of most cellulose nanofibers were about 20-30 nm and lengths were in hundreds nm range (Fig. 2). No significant differences were detected between the nanofibers from PT and HP poplar juvenile trees.

Figure 1. Nanofiber diameter distribution measured by dynamic light scattering.
Mechanical properties of PVA and its cellulosic composites

The elongation to break decreased in different percents of nanofibers and MCC for all composites compared with pure PVA. This indicated that the toughness of PVA increased by adding these cellulose because the elongation is related to the toughness of a material. The tensile modulus and strength of neat PVA and its composites reinforced by MCC and nanofibers form MCC, hybrid poplar (HP), and _P. trichocarpa_ (PT) with 1, 2, and 5 % are shown in Figures 3 and 4, respectively. Generally, the small nanofibers reinforced PVA composites had much higher mechanical properties (both modulus and strength) than those of neat PVA and MCC reinforced composites. This may be because small nanofiber had higher mechanical properties and higher aspect ratio (length/diameter) than those of MCC (Cheng and Wang 2008, Cheng et al. 2009 a, b). The tensile modulus of neat PVA was decreased by untreated MCC, but not significantly different (P-values between 0.07 to 0.90). PVA modulus was increased by all cellulosic nanofibers, which was not significant for 1% nanofibers (P=0.12), but was significantly increased by 2% (P=0.01) and 5% (P=0.002). There was no dramatic difference between 2% and 5% nanofiber reinforced composites. And no big differences were detected between the two nanofibers from HP and PT, which indicated that the nanofibers from HP and PT could have similar structures and dimensions.
The tensile strength of neat PVA was significantly decreased by all the three contents of MCC, (P=0.002 for 1%, P=0.003 for 2%, and P=0.007 for 5%). However, PVA strength was not decreased by all cellulosic nanofibers. There was no difference among them (P values between 0.09 to 0.64). The maximum modulus improvement of PVA was about 38% by 5% nanofiber (Figure 3).

**Thermal degradation behaviors of PVA and its cellulosic composites**

The TGA curves of neat PVA, neat HP nanofibers, HP wood, and HP nanofiber reinforced composites shown in Figure 5. The thermal degradation behavior of pure PVA film showed the weight loss starting at its melting point (typically 226 °C) and has a very narrow temperature range.
range of degradation. Pure nanofibers started to degrade at a lower temperature (~210 °C) than PVA, but show a very broad degradation temperature range. Similar findings were reported by others (Choi and Simonsen 2006). The degradation behaviors of all the nanocomposite films are generally between these those of neat PVA and nanofibers. The degradation temperature of HP wood was different when compared with neat nanofibers because the lignin and hemicelluloses play an important role on the degradation of wood and have different decomposition temperature ranges (Shafizadeh 1985).

*Figure 5. TGA curves for PVA, wood particles, nanofiber and its nanocomposites.*

The addition of cellulosic nanofibers increased the degradation temperature of PVA, showing an apparent increase in the thermal stability of the composite matrix. The decomposition peak temperature of the nanocomposites was clearly increased by cellulosic nanofibers. Figure 6 shows DTG curves of PVA and 2% and 5% HP nanofiber reinforced composites. The two nanocomposites show thermal events with a shift of ~9 °C and 14 °C toward higher temperature compared to the neat PVA. It is postulated that this phenomenon is due to interactions between the PVA and the nanofibers (Magalhaes et al. 2009). It indicated that only 2% cellulosic nanofibers can significantly improve PVA’s thermal stability.
Conclusions

Cellulose nanofibers can be isolated from hybrid poplar (HP) and *P. trichocarpa* (PT) using acid hydrolysis. Most of nanofibers were bundles of single nanocrystals and the average diameter of the nanofibers was about 21 nm measured by DLS and AFM. The nanofibers can be used to reinforce PVA to fabricate bio-nanocomposites. Cellulose nanofibers had much better performance than commercial MCC for PVA reinforcement. No significant differences of tensile mechanical properties of PVA nanocomposites reinforced with cellulosic nanofibers isolated from HP and PT were detected. The decomposition temperatures of the cellulosic nanocomposites were higher than that of neat PVA, indicating that the thermal degradation behavior of PVA was improved by cellulosic nanofibers.

References


