



Fabrication and properties of transparent polymethylmethacrylate/cellulose nanocrystals composites

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ARTICLE INFO

Article history:

Received 20 August 2009
Received in revised form 8 February 2010
Accepted 9 February 2010
Available online 4 March 2010

Keywords:

Cellulose nanocrystals
Acid-hydrolysis
High-pressure homogenization
Polymethylmethacrylate
Nanocomposites

ABSTRACT

Nano-sized cellulose crystals were fabricated from microcrystalline cellulose (MCC) using combined sulfuric acid hydrolysis and high-pressure homogenization techniques. The crystals were then utilized to prepare polymethylmethacrylate (PMMA) nanocomposites by the solution casting method. The cellulose nanocrystals had diameters from about 8 to 10 nm and lengths in the range of 60–120 nm. Wide-angle X-ray diffraction (WXR) results on the freeze-dried crystals revealed a slight increase in the degree of crystallinity after acid treatment. The composite sheets retained good transparency due to the size effect and dispersion of the cellulose nanocrystals. The thermogravimetric analysis indicated retained thermal stability of the composites. The storage modulus of the nanocomposite sheets from dynamic mechanical analysis showed significantly enhanced property in comparison with that of the pure PMMA sheets. The glass transition of the nanocomposites was shifted to lower temperatures with respect to the pure PMMA material.

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1. Introduction

Cellulose is one of the most abundant materials in nature, which mainly comes from plants (e.g., wood and cotton) and a variety of other natural products including bacteria and tunicates (Heux et al., 2000). Cellulose fibers exhibit a unique structural hierarchy derived from their biological origin. They are composed of assemblies of microfibrils (OSullivan, 1997), which form slender and nearly endless rods. Through acid and/or enzymatic hydrolysis, these microfibrils break down into short crystalline rods or “cellulose micro/nano-crystals.” With a very high modulus of elasticity, estimated to be 138 GPa (Nishino et al., 1995) for the crystalline phase and a calculated specific-surface-area of several hundreds of m²/g, low-cost, low density, low energy consumption, easy processability, renewable nature, and recyclability, cellulose nanocrystals have attracted considerable attention for exploring new applications. They have the potential for significant reinforcement of polymers at low filler loading levels (Dubief et al., 1999; Dufresne, 2003). Both natural and synthetic polymers were reported as matrix material. Natural polymers used include poly(β -hydroxyoctanoate) (Dufresne et al., 1999), starch (Angles and Dufresne, 2000), and cellulose acetate butyrate (Grunert and Winter, 2002). Synthetic polymers including poly(styrene-co-butyl acrylate) (Favier et al., 1995; Helbert et al., 1996), poly(vinyl chloride) (Chazeau

et al., 1999), waterborne epoxy (Ruiz et al., 2001), polycaprolactone (Samir et al., 2005; Siqueira et al., 2009), polyurethane (Cao et al., 2007; Marcovich et al., 2006), and polyfurfuryl alcohol (Pranger and Tannenbaum, 2008) have also been used.

Recently, many transparent polymeric materials such as polycarbonate, poly(methyl methacrylate), polystyrene, and poly(vinyl chloride) have been widely used as optical materials because of their excellent optical clarity and lower density. However, these polymers exhibit relatively low strength, which limit their structural application. Some research interests were concentrated on the formation of strong, but transparent polymer composites using bacterial cellulose (BC) (Iwamoto et al., 2005; Nogi et al., 2005, 2006). They showed improvements in both strength and transparency through isolating nanofibrillated cellulose structures, excluding larger diameter cellulosic fibers, and improving the distribution of the nanofibers in the matrix (Shimazaki et al., 2007; Yano et al., 2005). For example, BC nanofibers were acetylated to enhance the properties of optically transparent composites of acrylic resin reinforced with the nanofibers (Ifuku et al., 2007). BC nanofibers acetylated from degree-of-substitution (DS) of 0–1.76 were obtained. Since acetylation decreased the refractive index of cellulose, regular transmittance of composites comprised of 63% BC nanofibers was improved, and deterioration at 580 nm was suppressed to only 3.4% because of fiber reinforcement. Microcrystalline cellulose (MCC) is aggregated crystallites; and further processing of MCC to produce nanocrystals provides a potential way to generate reinforcement nanomaterial for optical resins.

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Polymethylmethacrylate (PMMA) is one of the important transparent commercial plastics, which has been utilized to make windows, lenses, and other optical devices. Its application has been restricted by its relatively low mechanical properties. Many attempts have been made to enhance its performance. Reinforcements with nano-particles (Ayre and Bucknall, 1998; Messaddeq et al., 1999; Nussbaumer et al., 2003) and micro-sized fibers (Chen et al., 2009; Kudoh et al., 1996; Olson et al., 1992; Tang et al., 2006) are shown to be effective techniques. Some improvements in mechanical properties are recognizable. However, very limited research has been reported on using cellulose crystals as reinforcement material. In this work, PMMA nanocomposites reinforced by nano-sized cellulose crystals were presented. Cellulose nanocrystals were manufactured from MCC by acid-hydrolysis combined with high-pressure homogenization. Nano-sized cellulose crystals were incorporated into dimethylformamide (DMF) to obtain a stable suspension, and then introduced into PMMA, and the nanocomposite sheets were prepared by solution casting and thermal curing. The objectives of the study were to study the effect of high-pressure homogenization treatment on the morphology and size of the manufactured crystals, and to investigate thermal and mechanical performance of the PMMA-based nanocomposites.

2. Methods

2.1. Material

Microcrystalline cellulose (Avicel FD-100 MCC, FMC Biopolymer, Philadelphia, PA, USA) was selected as raw material for producing the cellulose nanocrystals. Sulfuric acid (95–98 wt.%, VMR, West Chester, PA, USA), *N,N*-dimethylformamide (DMF) (Sigma-Aldrich, St. Louis, MO, USA), and poly(methyl methacrylate) (PMMA) ($M_w = 75,000$, Polysciences Inc., Warrington, PA, USA) were analytical grade and used as received without further purification.

2.2. Preparation of the cellulose nanocrystals (CNs)

Forty grams of MCC were mixed with 64 wt.% sulfuric acid aqueous solution (700 ml) and the mixture was stirred vigorously at 45 °C for 3 h. Five-fold dilution was then applied to the mixture to stop the hydrolysis reaction. The suspension was centrifuged at 12,000 rpm for 10 min (Sorvall RC-5B Refrigerated Superspeed Centrifuge, Du Pont Instrument) to separate the crystals in the suspension. The crystals were then washed with distilled water; and the mixture was centrifuged and the crystals separated again. The process was repeated five times for each sample. The precipitate was finally placed in regenerated cellulose dialysis tubes (Fisher Scientific, Pittsburgh, PA, USA) having a molecular weight cutoff of 12,000–14,000 and dialyzed against distilled water for several days until the water pH reached a value of 7.0. The obtained material was designated as acid-hydrolyzed MCC (HMCC).

To further reduce the size of the cellulose crystals, mechanical treatment was applied for the chemically treated samples. The suspension of cellulose crystals was processed through a high-pressure homogenizer (Microfluidizer M-110P, Microfluidics Corp., Newton, MA, USA) with a pair of Z-shaped interaction chambers (one 200 μm ceramic, and one 87 μm diamond) under an operating pressure of 207 MPa. A sample was taken after each pass through the homogenizer, designated as CNs-pass number. After five passes, the suspension was collected and dried using a freeze-dryer (FreeZone, 2.5 plus, Labconco Corp., Kansas City, MO, USA) to obtain dry cellulose crystals (i.e., CNs-5).

2.3. Preparation of the PMMA/CNs nanocomposites

PMMA was dissolved in DMF solution to prepare a mixture with a concentration of 20 mg/ml. Separately, freeze-dried cellulose nanocrystals powder (i.e., CNs-5) was added into DMF solution and the mixture was ultra-sonicated for several hours to obtain a homogeneous stable suspension. The suspensions of the CNs-5 and PMMA with DMF were then mixed in target weight ratios for achieving final dry composites containing 0–10 wt.% of solid cellulose nanocrystals in the PMMA matrix. The resulting mixtures were strongly stirred to achieve a good dispersion of CNs in the polymer matrix. Finally, the solution was cast in glass Petri dishes and dried in an oven at 60 °C for 48 h, and 75 °C for 10 h. By using cellulose nanocrystals at the loading levels of 0, 2, 3, 5, 8 and 10 wt.%, a series of composite sheets with a thickness of about 0.7 mm was prepared. The composite samples were designated as PMMA, PMMA/CNs-2, PMMA/CNs-3, PMMA/CNs-5, PMMA/CNs-8, and PMMA/CNs-10, respectively. Test samples were machined from the manufactured composite sheets.

2.4. Characterization of cellulose crystals and PMMA/CNs nanocomposites

The morphology of untreated MCC powder was observed with scanning electron microscopy (SEM) (S-3600 N, Hitachi, Japan) at 25 kV. The MCC powders were pasted onto a metal stub and coated with a thin layer of gold. The morphology of chemically and mechanically treated cellulose crystals was characterized by transmission electron microscopy (TEM) (JEOL 100CX, JEOL USA, Inc.), using an acceleration voltage of 80 kV. A drop (5 μl) of a diluted suspension of CNs was deposited on a 400-mesh carbon-coated copper grid. The material was allowed to dry and then stained with uranyl acetate to improve the contrast. The distribution of nanocrystal dimensions was obtained from the analysis of TEM images using the Adobe Photoshop software. Fifty nanocrystals were randomly selected and measured by the ruler tool in each image.

Wide-angle X-ray diffraction (WXR) patterns of the raw MCC and manufactured CNs were recorded by Bruker Siemens D5000 X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. X-ray diffraction data were collected from $2\theta = 5$ – 40° in steps of 0.02° at room temperature; and were further analyzed using the MDI Jade 5.0 software (Materials Data, Inc.). The diffuse halo due to the amorphous regions of the cellulose was subtracted by choosing a software-generated parabolic background function. Curve-fitting was performed to find individual peak region. Resulting main diffraction peaks were integrated and used to calculate the crystallinity (Cr, %) of the (2 0 0) plane using:

$$\text{Cr (\%)} = 100\% \left(\frac{A_{200}}{A_{\text{total}}} \right) \quad (1)$$

where A_{200} and A_{total} are the integrated area of the peak assigned to (2 0 0) planes and of the whole diffraction zone. The Scherrer equation was also used to calculate the crystal thickness, D (nm), by

$$D = K\lambda / (B \cos \theta) \quad (2)$$

where λ is the radiation wavelength, θ is the diffraction angle in radians, and B (nm) is the full width of the diffraction peak measured at the half maximum height prior to smoothing. The correction factor, K , was taken to be 0.9. Before plotting, data were smoothed over 35 adjacent points and were then normalized so that the main peaks have the same y -axis values and can be compared directly.

X-ray photoelectron spectroscopy (XPS) was performed on manufactured CNs using a Shimadzu Kratos Axis-165 Spectrometer with a monochromatic MgK α source (1253.6 eV) at 15 kV and 20 mA. The freeze-dried CNs-5 powder was mounted onto a holder

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