Fabrication and properties of transparent polymethylmethacrylate/cellulose nanocrystals composites

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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 (WXRD) 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.

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 nano-crystals 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 (Samar 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 (Iluku 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.
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) (Mw = 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 potted 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 (WXRD) patterns of the raw MCC and manufactured CNs were recorded by Bruker Siemens D5000 X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA. X-ray diffraction data were collected from 2θ = 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:

\[
Cr \% = \frac{A_{200}}{A_{total}} \times 100 \%
\]

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

\[
D = \frac{K \lambda}{(B \cos \theta)}
\]

where \(\lambda\) is the radiation wavelength, \(\theta\) 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 MgKa source (1253.6 eV) at 15 kV and 20 mA. The freeze-dried CNs-5 powder was mounted onto a holder.
with a piece of double-sided adhesive tape and the prepared sample was placed in a vacuum in the range of $1 \text{–} 5 \times 10^{-8}$ torr. The atomic percentages of the elements present were derived from a high-resolution spectra run with pass energy of 48 eV and an increment of 0.1 eV.

The optical transmittances of the PMMA and PMMA/CNs sheets were measured at wavelength from 400 to 1000 nm using a UV–vis spectrophotometer (Model UV-1601, Shimadzu Corp., Japan). Transmission spectra were measured using air as reference. The morphology of the CNs in the composite was observed using a High-resolution Transmission Electron Microscope (HRTEM) (JEOL 2010, JEOL USA, Inc.). A drop of the PMMA-DMF solution (5 µl) with 2 wt.% CNs was deposited on a carbon-coated copper grid. The material was allowed to dry and stained using uranyl acetate for observation. Thermogravimetric analysis (TGA) of the PMMA and PMMA/CNs composites was carried out with a TA Q50 (TA Instrument Inc., New Castle, DE, USA). The samples about 5 mg were heated from 30 to 550 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 mL min$^{-1}$. Differential scanning calorimetry (DSC) experiments were carried out with a TA Q100 differential scanning calorimeter (TA Instrument Inc., New Castle, DE, USA). The samples were heated from room temperature to 165 °C to remove any possible residue solvent, cooled to 30 °C, and then heated to 200 °C at the same heating ramp of 10 °C/min under nitrogen atmosphere. The data were collected on the second heating ramp. Glass transition temperatures ($T_g$) were determined from the inflection point in the heat flow versus temperature curves. Dynamic mechanical analysis (DMA) of the PMMA/CNs composite sheets was carried out using a dual-cantilever mode with a TA Q800 analyzer (TA Instrument Inc., New Castle, DE, USA). The measurements were performed from room temperature to 160 °C at a constant frequency of 1 Hz, strain amplitude of 0.01%, and heating rate of 2 °C min$^{-1}$. Four replicate samples with dimensions of 35.0 mm in length, 12.7 ± 0.1 mm in width, and 0.7 ± 0.05 mm in thickness, were used to characterize each type of the sheets.

3. Results and discussion

3.1. Morphological property of MCC/CNs and their suspensions

![Fig. 1](image1.jpg)

**Fig. 1.** Photograph of aqueous suspensions from MCC, HMCC, and CNs with 1 through 5 homogenizing cycles.

![Fig. 2](image2.jpg)

**Fig. 2.** SEM micrograph of the raw microcrystalline cellulose (MCC).

![Fig. 3](image3.jpg)

**Fig. 3.** TEM micrographs of HMCC (a) and CNs (b, c, and d representing CNs with 1, 3, and 5 homogenizing cycles, respectively).

(CNs) passed through the homogenizer for 1–5 cycles. Raw MCC precipitated at the bottom of the test tube in a short time after being added into water. The HMCC formed a stable opalescent suspension in water. By homogenizing these acid-hydrolyzed cellulose nanocrystals under high pressure (i.e., 207 MPa), the obtained CNs well dispersed in water without visible aggregation. The light blue transparent suspension was formed as shown by the samples “1” through “5”, which reflected the nano-sized particles in the suspensions.

The morphology of raw MCC dry powder observed by SEM is shown in Fig. 2. Large agglomerates with around 30 μm in length were observed. In fact, it is reported that these large sized MCC granules are composed of strong hydrogen bonding microfibrils (Eichhorn and Young, 2001). After acid hydrolysis and mechanical treatments, individual crystals were obtained. Fig. 3 shows selected TEM images of the manufactured CNs. The size distribution of the nanocrystals was analyzed and the result is plotted in Fig. 4. HMCC presented many crystalline whiskers with the length of more than 100 nm. The apparent agglomeration of the crystals still existed, probably due to the surface ionic charge caused by strong acid treatment. The number average crystal length and diameter were, respectively 125 ± 28 nm and 8.1 ± 1.9 nm for the HMCC (aspect ratio = 15.4). High pressure treatment effectively dispersed the aggregated crystals by strong mechanical shearing forces. Spindle-shaped cellulose nanocrystals presented a relative uniform size. The homogenized samples showed a decreased crystal length and with increased treatment cycles. High-pressure homogenized cellulose nanocrystals CN1, CN3, and CN5 had the average lengths of 113 ± 25 nm, 94 ± 22 nm, and 62 ± 26 nm; and average diameters of 8.5 ± 1.8 nm, 9.5 ± 1.8 nm, and 8.7 ± 1.2 nm, respectively. And the corresponding aspect ratios of the CN1, CN3, and CN5 were 13.3, 9.9, and 7.2, respectively. The length distribution data (Fig. 4) clearly shows a shift toward smaller dimensions as the treatment cycle increased. It is thus illustrated that the high-pressure homogenizer treatment can effectively reduce the length of the cellulose crystals and disperse them in aqueous suspension.

Certain degree of sulfation may exist in the hydrolyzed cellulose crystals due to strong sulfate acid treatment, which may affect particle separation in the dispersion. Roman and Winter (2004) used a chemical titration method to determine the degree of sulfation in acid-treated MCC. It was concluded that certain sulfate groups were introduced on the treated MCC surfaces. Fig. 5 shows results of the XPS measurement from this work. As shown, peaks centered at the 532.1 eV and 288.0 eV positions were attributed to O1s and C1s, respectively. There was no peak at the 165 eV position (ascribed to S 2p). The data indicate that no detectable sulfur element existed in the manufactured CNs from this work. The binding energy peaks of the C1s at the 288.0 eV position show the carbons of the C=O group.

3.2. Crystallinity of MCC and CNs

WXRD spectra of MCC, HMCC, and CNs–5 are shown in Fig. 6. All the diffractograms showed a sharp peak around 20 = 22.5° and two
not well-defined peaks at $\sim 14.8^\circ$ and $\sim 16.5^\circ$, which are believed to represent typical cellulose I structure. Those patterns were fairly close to each other. However, MCC had the biggest crystal thickness ($D = 5.8$ nm), while HMCC and CNs-5 had smaller ones ($D = 5.2$ nm and 4.8 nm, respectively). They presented the cross-sectional measurements perpendicular to the (2 0 0) planes. Therefore, crystallite dimension of samples decreased somewhat after treatments. It should be pointed out that there is a difference between measured crystal diameter from TEM images and XRD calculation of the crystal thickness. This difference was a result of the TEM measurement technique and selection of the crystals for measurements. Smaller crystals in the distribution cannot be effectively selected and measured by the TEM technique.

The crystallinity of MCC and HMCC samples were found to be 58% and 65%, respectively, which are in typical crystallinity value range of 55–80% (Wei et al., 1996). It was thought that the contribution of crystalline peak areas increased after acid hydrolysis because the amorphous regions of the MCC were more susceptible to acid attack. However, the diffraction patterns indicated the presence of an unneglectable volume of remaining amorphous cellulose. The crystallinity of the CNs-5 was fairly close to that of HMCC. Although the detailed information of the peaks assigned to (1 1 0), (1 1 0) and (0 0 4) planes was not presented, it is clearly shown in Fig. 5 that those peaks were not obviously weaker or absent, indicating that the essential of cellulose crystals was not significantly changed by the treatments.

### 3.3. Appearance, morphology, and optical transmittance of the PMMA/CNs nanocomposites

Fig. 7a shows photographs of the PMMA/CNs composite sheets with 0, 2, 3, 5, 8, and 10 wt.% CNs, respectively. The pattern and letters in the background can be clearly seen through the sheet, indicating that the nanocomposite sheets were transparent. However,

Fig. 7b shows the details of the crystal distribution in the PMMA matrix, where the stained cellulose crystals are in dark color and the PMMA matrix is in gray color. There is a certain degree of nanocrystal agglomeration regardless of the good dispersion in the solution stage. The CNs can disperse well in aqueous systems, but some agglomeration always happens in other polarized organic solvents because of the hydrophilic nature of cellulose. After all, at low loading level (less than 3%) the composite still had a high optical transmittance (more than 50%), which can be used as a good optical resin.

3.4. Thermal, mechanical properties of the PMMA/CNs nanocomposites

Fig. 9 shows the TG and DTG curves of the pure PMMA and PMMA/CNs nanocomposites. According to the DTG curves, the degradation of the nanocomposites can be divided into two processes, which are ascribed to the decomposition of cellulose nanocrystals (150–250 °C) and PMMA (300–450 °C), respectively. The nanocomposites began to degrade at a slightly lower temperature than that of pure PMMA. The weight loss of the nanocomposites in the temperature range up to 300 °C was slightly higher (about 5 wt.%) than that of pure PMMA. As listed in Table 1, the maximum decomposition temperature was increased 5–15 °C with the variation of the content of cellulose nanocrystals in the nanocomposites.

Fig. 10 shows the DSC thermograms of PMMA and its nanocomposites filled with different contents of CNs. No obvious crystalline peak of cellulose crystals of PMMA was observed in the DSC curves. Glass transition temperature ($T_g$) was taken as the midpoint of the endothermic transition. The values of $T_g$ for PMMA, PMMA/CNs-2, PMMA/CNs-3, PMMA/CNs-5, PMMA/CNs-8, and PMMA/CNs-10 were 91.4, 88.6, 71.3, 72.3, 69.9, and 71.6 °C, respectively. The $T_g$ values of the nanocomposites were lower than that of PMMA. With more than 2 wt.% cellulose nanocrystals in the composites, the nanocomposites showed their $T_g$ at about 70 °C. The trend of glass transition shifted to a lower temperature suggested an increase of the mobility of polymer chains. The presence of cellulose nanocrystals can induce a restricted mobility of polymer chains by forming hydrogen bonds in the interface, thus interrupting the dominant original interactions among the matrix polymer chains.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>First process</th>
<th>Second process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset temperature (°C)</td>
<td>$T_{max}$ (°C)</td>
</tr>
<tr>
<td>PMMA</td>
<td>161.0</td>
<td>183.1</td>
</tr>
<tr>
<td>PMMA/CNs-2</td>
<td>146.2</td>
<td>172.2</td>
</tr>
<tr>
<td>PMMA/CNs-3</td>
<td>139.5</td>
<td>186.9</td>
</tr>
<tr>
<td>PMMA/CNs-5</td>
<td>138.6</td>
<td>178.0</td>
</tr>
<tr>
<td>PMMA/CNs-8</td>
<td>147.9</td>
<td>192.0</td>
</tr>
<tr>
<td>PMMA/CNs-10</td>
<td>144.3</td>
<td>184.6</td>
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</table>

Fig. 9. TGA (a) and DTG (b) curves of the PMMA, CNs, and PMMA/CNs composites.

The UV–vis transmittance spectra of the pure PMMA matrix and PMMA/CNs composite sheets at visible wavelength range of 400–800 nm are shown in Fig. 8. The average transmittance of the composite with 2 wt.% CNs was 60%, which is slightly lower than that of previously reported BC nanofibers reinforced composites (Nogi et al., 2005). The transmittance of PMMA/CNs nanocomposite was reduced with the increase of the loading content of cellulose nanocrystals, because of the heterogeneous nature of the composites. The optical transmittance of the cellulose crystalline composites is largely dependent on the dispersion of crystals in the matrix.

Onset temperature and $T_{max}$ (degradation temperature) of pure PMMA and PMMA/CNs composites with CNs-5 weight content of 2%, 3%, 5%, 8% and 10%.

The samples with increased cellulose crystal loading levels became increased opalescent due to nanocrystal agglomeration as shown by the TEM micrograph of the PMMA/CNs composite (Fig. 7b). The UV–vis transmittance spectra of the pure PMMA matrix and PMMA/CNs composite sheets at visible wavelength range of 400–800 nm are shown in Fig. 8. The average transmittance of the composite with 2 wt.% CNs was 60%, which is slightly lower than that of previously reported BC nanofibers reinforced composites (Nogi et al., 2005). The transmittance of PMMA/CNs nanocomposite was reduced with the increase of the loading content of cellulose nanocrystals, because of the heterogeneous nature of the composites. The optical transmittance of the cellulose crystalline composites is largely dependent on the dispersion of crystals in the matrix.
4. Conclusions

PMMA composites were successfully prepared by solution casting with the reinforcement of cellulose nanocrystals manufactured from MCC using sulfuric acid-hydrolysis combined with high-pressure homogenization techniques. Cellulose nanocrystals with an average length of 124 nm and an average diameter of 8–10 nm were obtained by acid-hydrolysis alone. The crystals were further shortened to about 62 nm through five high-pressure homogenization techniques. Cellulose nanocrystals with an average length of 124 nm and an average diameter of 8–10 nm were obtained by acid-hydrolysis alone. The crystals were further shortened to about 62 nm through five high-pressure homogenization techniques. Cellulose nanocrystals with an average length of 124 nm and an average diameter of 8–10 nm were obtained by acid-hydrolysis alone. The crystals were further shortened to about 62 nm through five high-pressure homogenization techniques. Cellulose nanocrystals with an average length of 124 nm and an average diameter of 8–10 nm were obtained by acid-hydrolysis alone. The crystals were further shortened to about 62 nm through five high-pressure homogenization techniques. Cellulose nanocrystals with an average length of 124 nm and an average diameter of 8–10 nm were obtained by acid-hydrolysis alone. The crystals were further shortened to about 62 nm through five high-pressure homogenization techniques.

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References


Kudoh, H., Sasuga, T., Seguchi, T., Katsuura, Y., 1996. High energy ion irradiation effects on polymer materials. 2 Proton irradiation effects on PMMA and GFRP. Polymer 37, 4663–4665.


