Acrylic Functionalization of Cellulose Nanocrystals with 2-Isocyanatoethyl Methacrylate and Formation of Composites with Poly(methyl methacrylate)

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ABSTRACT: Cellulose nanocrystals (CNCs) derived from renewable plant-based materials exhibit strong potential for improving properties of polymers by their dispersal in the polymer matrix as a composite phase. However, the hydrophilicity and low thermal stability of CNCs lead to compromised particle dispersibility in common polymers and limit the processing conditions of polymer-CNC composites, respectively. One route that has been explored is the modification of CNCs to alter surface chemistry. Acrylic materials are used in a broad class of polymers and copolymers with wide commercial applications. Yet, the available methods for adding groups that react with acrylics to enhance dispersion are quite limited. In this work, a versatile chemical modification route is described that introduces acryloyl functional groups on CNCs that can in turn be polymerized in subsequent steps to create acrylic−CNC composites. The hydroxyl group on CNC surfaces was reacted with the isocyanate moiety on 2-isocyanatoethyl methacrylate (IEM), a bifunctional molecule possessing both the isocyanate group and acryloyl group. The resulting modified CNCs (mCNCs) showed enhanced hydrophobicity and dispersibility in organic solvent relative to unmodified CNCs. Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy, solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis verified the surface modification and allowed an estimation of the degree of modification as high as 0.4 (26.7% surface hydroxyl substitution CNC). The modified CNCs were copolymerized with methyl methacrylate, and the composites had improved dispersion relative to composites with unmodified CNCs and enhanced (104%) tensile strength at 2 wt % CNC when compared to the neat poly(methyl methacrylate) (PMMA), indicating a benefit of the reactive acryloyl groups added to the CNC surface. Overall, the modification strategy was successful in functionalizing CNCs, opening possibilities for their use in organic media and matrices.

INTRODUCTION

Cellulose is the most abundant renewable polymer produced in the world. For millennia, cellulose has been used as a raw material for applications in construction, paper, and textiles. These traditional applications took advantage of properties arising from the cellulose’s hierarchical structure; yet, it was not widely appreciated until the 1980s that nanocrystalline cellulose can be extracted when wood pulp cellulose fibers are subjected to controlled acid hydrolysis.1 Cellulose nanocrystals (CNCs) have attracted significant attention in the material community because of their exceptional physical and chemical properties.2,3 The main benefits of CNCs are their high strength and stiffness, lightweight relative to metals, low cost (relative to synthetic high-aspect nanoparticles like carbon nanotubes), anisotropic structure, renewability, and abundance. In addition, the native hydroxyl groups and charged sulfate groups produced during sulfuric acid hydrolysis facilitate water-based processing and interparticle network formation.4,5 CNCs have been proposed for applications in polymer composites, emulsion and foam stabilization, drug delivery, catalyst supports, and templating agents.6−12 Among polymers considered for composite applications, acrylics are one of the most common commercial polymers, used in applications including paints, construction materials, cosmetics, and dental treatment.13−15 Reinforcement of acrylic polymers with CNCs has been a subject of interest in recent years.16−20 However, the hydrophilicity of CNCs limits their homogenous dispersion in acrylic polymers. Therefore, there is interest in functionalizing CNC for compatibilization with acrylic polymers.21−23 Successful incorporation of CNCs into acrylic polymers has the potential to increase strength and/or stiffness without compromising transparency significantly.

Modification routes to produce functionalized CNCs have been summarized in recent reviews.24,25,29,32 These generally include physical adsorption or ion exchange of surfactants onto
the CNC surface as well as covalent attachment of molecules. However, such adsorption routes usually require extensive purification to remove excess surfactant, and ionic bonds are vulnerable to substitution via ion exchange in aqueous media. Covalent modifications of CNCs are more robust, and those explored include esterification, etherification, silylation, amidation, and urethanization (also known as carbamimation or carbanylation). For example, Ben Mabrouk et al. used methacryloxypropyl triethoxysilane (MPS) as a coupling agent to improve the compatibility between CNCs and acrylic polymer latex. Tan et al. modified cellulose nanofibers (CNFs) with an aminosilane and then added to a commercial waterborne acrylic/urethane coating. In that work, the CNFs were designed to disperse in an aqueous medium and then became physically incorporated into the coalescing polymer droplets during drying. Kedzior et al. grafted poly(methyl methacrylate) (PMMA) from the surface of CNC via free-radical polymerization with ceric ammonium nitrate as the initiator. In addition, the esterification of CNCs with bromoisobutryl bromide (BiB) has been utilized frequently to initiate atom transfer radical polymerization (ATRP) from the surface of CNCs. Meanwhile, the research concerning the addition of urethane groups onto the surface of CNCs is limited. The first modification of CNCs using isocyanate was reported in 2008 by Habibi and Dufresne who used toluylene-2,4-diisocyanate (TDI) to graft polycaprolactone (PCL) to CNCs. Siqueira et al. modified sisal-sourced CNCs with n-octadecyl, achieving a conversion of 7.8% available surface hydroxyl groups. Girouard et al. utilized the unequal reactivity of the two isocyanate groups in an isophorone diisocyanate (IPDI) monomer to introduce isocyanate functionality without chain extension. The modified CNCs showed enhanced thermal stability and reinforcing effect in polyurethane composites. To the best of our knowledge, the urethane functionalization of CNCs has not been exploited to introduce acrylic functionality. The introduction of an acrylic moiety via an isocyanate-functional acrylic molecule would allow an orthogonal two-step approach, where CNCs can be modified first via the isocyanate and stored for long periods prior to combining with acrylic and styrenic monomers and copolymerizing the acrylic moiety.

In this work, a chemical surface modification method was developed by grafting a single acrylic functional monomer to the CNC surface, via covalent bonding with a −OH group (Figure 1). This is accomplished by grafting acrylic monomers via an acrylic isocyanate, 2-isocyanatoethyl methacrylate (IEM). The chemical structures and proposed chemical reaction of the primary materials are shown in Figure 1. The acrylic-modified CNCs (mCNCs) are separated as a product with enhanced hydrophobicity and dispersibility in organic solvents. PMMA matrix composites containing mCNCs or unmodified CNCs (umCNCs) were prepared to understand the efficacy of the chemical modification approach. The enhanced mechanical performance of mCNC/PMMA composites with respect to umCNC/PMMA composites suggested a more homogeneous dispersion of mCNCs in the PMMA matrix. The method developed in this work is expected to be broadly applicable across many classes of acrylic, and styrenic via copolymerization, materials and cellulose-containing particles and polymers.

**RESULTS AND DISCUSSION**

**Characterizing the Chemistry of Modified CNCs.**

Figure 2 shows the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of umCNCs, mCNCs, and IEM. The umCNCs showed absorbance characteristic of cellulose functional groups, including the strong absorbances at 3000−3600 cm⁻¹ and multiple peaks around 900−1100 cm⁻¹, associated with −OH and −C−O−C− vibrations, respectively. In the spectra of IEM, two strong peaks were observed at 2240 and 1723 cm⁻¹, representing −N==C==O and −C==O stretching, respectively. A small peak at 1640 cm⁻¹ represented the alkenyl C==C stretch in IEM. Strong absorptions at 1723 and 1640 cm⁻¹ indicated the attachment of C==O and C==C groups on mCNCs. Concurrent with the disappearance of the −NCO peaks from IEM were the multiple absorption peaks between 1200 and 1700 cm⁻¹ associated with the formed urethane linkage between CNC and IEM. The small increment of the absorption between 2900 and 3000 cm⁻¹ also indicated the increased sp³ C−H stretch of the methyl group of IEM. The results suggested that the acrylic functional group has been attached to the CNC surface via a urethane linkage formed by the reaction between hydroxyl and isocyanate groups. Further support for the modification reaction was provided with X-ray
photoelectron spectroscopy (XPS) characterization. These results are included in the Supporting Information as Figure S1.

Solid-state $^{13}$C nuclear magnetic resonance (NMR) provided cross-polarized magic angle spinning (CP-MAS) spectra of umCNCs and mCNCs, as shown in Figure 3. The inset shows the corresponding chemical structure of mCNCs. Both spectra showed chemical shifts characteristic of the anhydroglucose units (AGUs) of cellulose, where typical peaks were displayed corresponding to C1 (105.2 ppm), C4$_{\text{cryst}}$ (89.2 ppm), C4$_{\text{amorph}}$ (83.8 ppm), C6$_{\text{cryst}}$ (65.4 ppm), and C6$_{\text{amorph}}$ (62.7 ppm). The resonances of C2, C3, and C5 of AGU were located closely between 70 and 80 ppm. After modification with IEM, six new peaks appeared as indicated in the inset, suggesting the attachment of vinyl groups (a and b at 127.9 and 136.2 ppm), carboxyl groups (d at 168.1 ppm), and urethane linkages (g at 157.3 ppm). Signals between 10 and 40 ppm were due to the hydrocarbons, specifically the secondary carbon (f at 40.1 ppm and e at 64.0 ppm; peak e was not visible because it is overlapped with C6) and primary carbon (c at 19.8 ppm). These results further support the surface modification of CNCs with IEM.

The degree of substitution (DS) was determined based on NMR spectra. DS is commonly used to quantify the extent of modification on CNCs. It is defined as the number of hydroxyl groups that have been modified per AGU, which ranges from 0 to 3.0 (with three hydroxyl groups on each AGU). The relative content of each carbon atom was represented by the integrated area under the corresponding signals. The DS was determined by

$$\text{DS} = \frac{C_{\text{IEM}}/N_{\text{IEM}}}{C_{\text{AGU}}/N_{\text{AGU}}}$$

where $C_{\text{IEM}}$ and $C_{\text{AGU}}$ represent the sum of the signal area of all carbon atoms in IEM and AGU, and $N_{\text{IEM}}$ and $N_{\text{AGU}}$ are the number of carbon atoms in IEM and AGU, respectively. The DS of mCNC was calculated to be 0.14. Meanwhile, because the hydroxyl groups on the CNC surface have easier access to reactive agent than that within CNCs, a modified DS is usually calculated to describe the extent of surface modification. Eyrey et al. provided an equation to calculate the number of hydroxyl groups on the CNC surface in moles per gram, which can be used to convert DS to the surface degree of substitution, $D_{\text{surface}}$. It is noted that the theoretical maximum $D_{\text{surface}}$ is 1.5 due to the crystalline structure of CNCs, where one C2, C3, and C6 hydroxyl group points out of the crystal surface for every two AGUs. The $D_{\text{surface}}$ was calculated to be 0.40 according to the dimensions of CNCs used in this work and the crystallographic parameter reported by Wu et al., which corresponds to 26.7% of available hydroxyl groups on CNCs. Elemental analysis on umCNC and mCNC further confirmed the modification reaction, and the data were also used to calculate the DS (Table 1). It was noted that the weight ratio of C/O (0.93) in umCNCs was higher than the theoretical ratio (0.9). Such differences are usually attributed to hydrocarbon impurities in the extracted CNCs. Nitrogen content in umCNCs was negligible. After the modification, the mCNCs contained 0.76 wt % nitrogen, consistent with the attachment of IEM on CNCs. The DS can be calculated by the following equations

$$Y = \frac{100M_{\text{IEM}} \times \text{DS}}{162 + W_{\text{N}} \times \text{DS}} = 100 \times \left( \frac{X_{\text{N}} \times M_{\text{IEM}}}{M_{\text{N}}} \right)$$

where $Y$ is the percent of substituted hydroxyl groups, $M_{\text{IEM}}$ is the molecular weight of IEM, $M_{\text{N}}$ is the atomic weight of nitrogen, and $W_{\text{N}}$ is the net increase in formula weight from adding one substituent group per AGU. The resulting DS was 0.10, and $D_{\text{surface}}$ is 0.28 based on elemental analysis. The discrepancies of the DS results between NMR and elemental analysis may have arisen from the different NMR signal sensitivity for each carbon atom in the samples. It was noted that the degree of substitution in this work was slightly higher than that (DS = 0.07) reported by Siqueira et al. for n-octadecyl isocyanate. Siqueira used more excess isocyanate, higher reaction temperature, but shorter reaction time, a different solvent (toluene), and no catalyst. Biyani et al. reported 0.59–0.96 for $D_{\text{surface}}$ with similar solvent and catalyst but different isocyanate agent and much harsher condition (100 °C for 16 h), based on UV–vis characterization. Girouard et al. achieved 1.4 for $D_{\text{surface}}$ with the same solvent and catalyst, but much more excess isocyanate (isophorone diisocyanate) agent and overnight reaction were used. In summary, this work achieved an intermediate level of DS with mild conditions compared with other research.

**Crystallinity of umCNCs and mCNCs.** X-ray diffraction (XRD) was used to examine the effect of surface modification on the CNC crystal structure (4) and is shown in Figure 4. The umCNCs showed typical peaks at 16.5, 22.5, and 34.5°, corresponding to the cellulose I structure. After the modification, the peaks at 34.5, 39.2, and 47.5° showed

|     | umCNC | mCNC |
|-----|-------|------|
|     | 41.1  | 5.6  |
|     | <0.05 | 44.4 |
|     | 40.5  | 6.2  |
|     | 0.76  | 46.8 |

Note: Combustion elemental analysis was conducted. The C, H, and N contents were analyzed at 935 °C with a PerkinElmer 2400 Series II, and the O content was analyzed at 1000 °C with a Leco Truspec Analyzer.
evident reduction. The broadened peaks of mCNCs between 13 and 17° indicated a disrupted crystalline structure. The crystallinity index for umCNC and mCNC was calculated according to the method developed by Segal et al. As expected, the crystallinity index decreased from 91.4% for umCNCs to 76.5% after the modification (also corrected for the mass fraction of IEM in the IEM/CNC sample). This reduction is usually attributed to the disordered molecular arrangement of the crystalline part due to the surface. A reduction of the crystallinity index of modified CNCs was also reported by Kargarzadeh et al. and Siqueria et al.

**Thermal Stability of umCNCs and mCNCs.** Thermal stability of umCNC, mCNC, and washed mCNC was analyzed by thermogravimetric analysis (TGA). The weight loss curves and derivative weight loss curves of the samples are shown in Figure 5, and the degradation onset temperatures are shown in Table 2. The washed umCNC sample was prepared to isolate the effect of IEM modification from the multiple washing processes on mCNCs, which may affect the thermal stability of umCNCs. Both mCNCs and washed umCNCs showed early mass loss (~5%) at ~100 °C, which was attributed to the evaporation of residual toluene. The freeze-dried umCNCs showed a slightly lower onset temperature than mCNCs, with a difference of 6 °C, while the washing process decreased the onset temperature of umCNCs from 246 to 214 °C. This reduction in thermal stability may be due to the removal of residual sugar fragments from the surface of CNCs during multiple washing process. The adsorbed species are usually low-molecular-weight compounds that are generated by hydrolysis and condensed by freeze drying. It also demonstrated the enhanced thermal stability of mCNCs by comparing the washed umCNCs and mCNCs, which experienced the same washing processes. In addition, the thermal property of CNC/PMMA composites was examined by differential scanning calorimetry (DSC). The results show that the glass-transition temperature of CNC/PMMA composites was slightly lower than that of neat PMMA (Table S1). However, the difference between mCNCs/PMMA and umCNCs/PMMA is negligible.

**Enhanced Hydrophobicity and PMMA Compatibility of mCNCs.** Sessile drop water contact angle measurements were used to verify the change in wetting of mCNCs relative to umCNCs. Uniform films were prepared by drop-coating umCNCs (in water) or mCNC (in toluene) on a piranha-etched silicon wafer. The water contact angle on umCNCs (27 ± 2°) was only slightly higher than on the silicon wafer (20 ± 2°). After the modification with IEM, the water contact angle increased from 27° to 62 ± 2° (Figure S2). The reduced hydrophilicity upon IEM modification was consistent with expectations based on contact angles on acrylic materials, which range from 60 to 80° for PMMA. The change in wettability of the mCNCs could be correlated to the better dispersibility in a polar organic solvent, dimethylformamide (DMF), as shown in Figure 6. The umCNCs formed a turbid suspension in DMF after 2 h of sonication, while the mCNCs formed a clear suspension after mild agitation with a vortex mixer for 5 s. The mCNC suspension remained stable for at
least 2 weeks before copolymerization with methyl methacrylate.

We examined scanning electron microscope (SEM) images of neat PMMA and PMMA composites with 2 wt % mCNC and 2 wt % umCNC, shown in Figure S3. It is not possible to discern features that have obvious characteristics of the size or shape of individual CNCs, which is presumably a result of the similar electron density of PMMA and CNCs. However, at all three magnifications, the mCNC-containing samples (Figure S5d–f) have features well below ∼1 μm and appear to lack features consistent with the aggregation of CNCs. On the other hand, it is not obvious that the features in the umCNC–PMMA composites (Figure S5g–i), some of which are hundreds of nanometers to ∼1 μm, are CNC aggregates. Because of the difficulty in distinguishing CNCs from PMMA in SEM, we also utilized polarized light microscopy (PLM), which is a useful tool for analyzing CNC dispersions in a transparent, amorphous matrix. The crystalline nature of CNCs can give rise to birefringence when viewed under a crossed-polarizer light due to their optical anisotropy. Conversely, if the PLM images showed nonbirefringence, it can be concluded that the CNCs are well dispersed at this length scale. PLM also enables the assessment of dispersion on large scale, compared with electron microscopy techniques. Both bright-field (normal) and dark-field (PLM) images of umCNC and mCNC composites are shown in Figure 7. The mCNC composite showed dark images, suggesting an amorphous material and well-dispersed mCNC at this length scale. On the contrary, the umCNC composite showed birefringent regions across the observed area. This result indicated that umCNC tended to aggregate in the PMMA matrix with features on a scale from ∼5 to ∼40 μm, and CNCs are dispersed more homogeneously, indicating enhanced compatibility with the PMMA matrix.

**Mechanical Property Enhancement in PMMA.** The tensile strength of neat PMMA and mCNC/PMMA samples was measured with uniaxial tensile testing. The umCNC/PMMA film produced by compression molding was too brittle to be cut into specimens for testing. Therefore, the tensile strength of umCNC/PMMA was not reported here. All samples have a similar number averaged molecular weight of around 65 000 per gel permeation chromatography (Figure S4 and Table S2). Both neat PMMA and mCNC/PMMA samples were transparent, while umCNC/PMMA were only semitranslucent (Figure S5). Figure 8 shows the tensile strength values of the neat PMMA and mCNC/PMMA samples. The tensile strength of mCNC/PMMA (58.6 MPa) was 104% higher than that of neat PMMA (28.7 MPa). This result indicated good stress transfer in the composite. Additionally, the brittle nature and reduced transparency of the umCNC/PMMA film in comparison to those of the mCNC/PMMA film suggested that the mCNCs were dispersed more homogeneously than the umCNCs. Overall, these results suggested that the chemical modification scheme presented here provides an effective route to producing CNC composites with acrylic polymer matrices.

**METHODS**

**Materials.** Freeze-dried umCNCs were provided by the USDA Forest Products Laboratory and used as received. The CNCs were freeze-dried from an aqueous CNC suspension prepared from a mixed southern yellow pine dissolving pulp via a 64% sulfuric acid digestion, as described in detail elsewhere. The umCNCs were determined to contain 0.96% sulfur as residual sulfate esters. The counterion to the sulfate esters was Na+. The bifunctional modifier molecule, 2-isocyanatoethyl methacrylate (IEM), was purchased from TCI America, stabilized with butyl hydroxytoluene at >98% purity. Dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), dimethylformamide (DMF, anhydrous, 99.8%), benzy1 peroxide (BPO, Luperox A98) and isocyanate catalyst, dibutyltin dilaurate (DBTDL), were purchased from Sigma-Aldrich and used as received. Molecular sieves (MS, type 3A, EMD Millipore MX 1583D-1) and toluene (ACS, 99.5%) were purchased from Alfa Aesar and used as received.

**Preparation of IEM-CNC.** The umCNCs (0.4 g) were first mixed with anhydrous DMSO (17 g) in a 40 mL glass vial by vortex mixing. DMSO was dried by molecular sieves for 1 h before using. The concentration of umCNCs in DMSO was ∼2.3 wt %. The suspension of CNCs was then sonicated for 1.5 h in a 2510 Branson bath sonicator. After the sonication, the suspension appeared transparent, which indicated that the CNCs were dispersed homogeneously in DMSO. The suspension was then heated to 60 °C with magnetic stirring. Next, IEM (2.5 g) was added into a separate glass vial to premix with DBTDL (30 μL). The IEM was added in excess at a molar ratio of IEM to anhydroglucose units (AGUs) of CNCs as 6.5:1. The IEM/DBTDL mixture was added dropwise into the CNC/DMSO suspension. The reaction was then carried out at 60 C for 2 h. After the reaction was completed, the mixture was separated into four equal parts.

![Figure 7. Polarized light microscopy (dark field) indicates well-dispersed mCNCs and large aggregates of umCNCs in the PMMA matrix. The scale bar is 100 μm.](image-url)
Each part was precipitated and washed with toluene and centrifuged at 3000 rpm for 10 min. This process was repeated three times. The IEM-modified CNC (mCNC) settled at the bottom of the vial forming a smooth and clear organogel (mCNC/toluene). This organogel was vacuum-dried at 50 °C for 24 h to get mCNCs.

Preparation of PMMA/CNC Nanocomposite. PMMA composites were prepared with both umCNC and mCNC via identical yet separate procedures. PMMA was polymerized in situ with CNCs in DMF to synthesize the nanocomposites at a filler loading of 2 wt %. First, umCNCs or mCNCs were dispersed in DMF and sonicated for 1 h. MMA was added by two equal parts to a final concentration of 0.25 g/mL. The two-step addition of MMA aimed to allow the first half of the added MMA to react with mCNC, prior to adding the remaining MMA. The first half of MMA was added to the DMF suspension along with BPO. The molar ratio between BPO and total MMA was kept as 1:1000. The mixture was then transferred into a three-neck flask heated with an oil bath. The flask was heated to 80 °C under mechanical stirring with a Cramrof Compact Digital Lab Mixer and refluxed under a flowing nitrogen. After 1 h of reaction, the second half of MMA was added dropwise by a separatory funnel within 0.5 h. The reaction continued for 5.5 h. The resulting polymer solution was poured into excess DI water with vigorous magnetic stirring, and the nanocomposites were precipitated and filtered. The solid samples were washed three times with DI water. The resulting samples were dried in a convection oven at 80 °C for 12 h before being hot-pressed into a 0.6 mm thick film by a Carver Hydraulic Hot Press System. Composite samples were hot-pressed at 120 °C for 30 min under a load of 2 tons. Samples were released after the temperature was water-cooled down to 50 °C. Neat PMMA was also prepared with the same procedure for comparison.

Characterization. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). umCNCs, mCNCs, and IEM were analyzed by ATR-FTIR to characterize their chemical structures (Bruker Vertex 80 V spectrometer with a Bruker Platinum ATR accessory). The wavenumber scan range was from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹ and a total of 64 scans. For the umCNCs and mCNCs, the spectra were normalized at the 1060 cm⁻¹ peak since this absorbance was associated with ether groups, which were assumed to not participate in the reaction.

X-ray Photoelectron Spectroscopy (XPS). Both umCNCs and mCNCs were analyzed using a Thermo K-Alpha X-ray photoelectron spectrometer. Powder form samples were radiated with monochromatized Al Kα (1486.7 eV) radiation with a 45° take-off angle, a 400 μm beam size, and 50 W power. The chemical shifts were taken from the literature, and the spectra were calibrated by setting the C=C contribution in the C 1s emission to 285.0 eV.

Solid-State ¹³C NMR. The chemical structure of umCNCs and mCNCs was characterized by solid-state ¹³C NMR. The degree of substitution of IEM was also determined from NMR. Approximately 50 mg of umCNC or mCNC was packed into a 24 mm OD MAS rotor. CP-MAS spectra were recorded using a Bruker AV3-400 NMR spectrometer operating at a H frequency of 400 MHz. A dual-channel BB-MAS probe was operated at a spinning speed of 10 kHz. Cross-polarization was achieved with a trapezoidal-shaped contact pulse for H varying in power from 70 to 100% and a length of 2 ms. Repetition delay between scans was 4 s, and at least 12 000 scans were acquired for each sample to measure spectra. The spectra were normalized by the peak positioned at δ = 75 ppm, an absorbance that was attributed to the C2, C3, and C5 carbons in the crystalline cellulose, which were assumed to not participate in the reaction.

Elemental Analysis. Combustion elemental analysis was conducted by ALS Environmental (Tucson, AZ) for both umCNC and mCNC samples. The samples were analyzed for C, H, O, and N contents. The C, H, and N contents were analyzed with a PerkinElmer 2400 Series II, and the O content was analyzed with a Leco Truspec Analyzer. The PerkinElmer instrument was calibrated with acetalalide, and the Leco Truspec was calibrated with benzylic acid. Approximately 2–5 mg of sample was weighed and then held in the combustion chamber for about 5 min. The oxygen analyzer was held at 1000 °C, and the C, H, and N analyzer was held at 935 °C. The degree of substitution was calculated based on the nitrogen content.

X-ray Diffraction (XRD). The crystalline structure of CNCs was examined with XRD analysis before and after modification. XRD analysis was performed on a Panalytical X-Pert Pro XRD system. Diffractograms were recorded over an angular range of 2θ = 5–70° and a step size of 0.008356° with Cu Kα (λ = 1.54 Å) radiation generated at an anode voltage and current of 45 kV and 40 mA, respectively.

Thermogravimetric Analysis (TGA). Thermal stability and changes in degradation associated with the modification step were assessed with TGA (TA Instruments TGA Q5000). Freeze-dried umCNC and mCNC were characterized. Compared to umCNCs, mCNC experienced four additional processes, including dispersion in DMF, surface modification, precipitation in toluene, and thermal drying. To isolate the effect of surface modification, freeze-dried umCNCs were treated with all processing steps as mCNCs with exception of the surface modification. The resulting sample is marked as “washed umCNC”. All samples were dried again at 50 °C for 24 h before testing. Samples were heated from 50 to 600 °C at a rate of 5 °C/min under a flowing nitrogen atmosphere. The onset temperature of degradation was determined by manually choosing points before and after the sharp drop on the weight loss curve and finding the intersection of the tangents at these two points.

Differential Scanning Calorimetry (DSC). The glass-transition temperature (Tg) of all samples was measured by DSC (TA Instruments DSC Q200). As a first step, samples were annealed in the instrument at 160 or 200 °C and then cooled to 0 °C at a rate of 20 °C/min. The samples were subsequently heated to 160 °C at a rate of 10 °C/min. This last heating step was used to obtain Tg of the sample. The value of Tg was assigned as the midpoint of the transition region of the heat flow curve using the instrument analysis software. Three tests were performed for each sample, and the average value and standard deviation were reported.

Contact Angle Measurement. To characterize the change of hydrophilicity of CNCs associated with the modification, contact angles of umCNCs and mCNCs were measured with DI water as the test liquid at 20 °C using a video contact angle system (Rame-Hart goniometer). The umCNC film was prepared by depositing drops of the aqueous umCNC suspension onto a piranha-cleaned silicon wafer, followed by drying at an ambient condition for 24 h. The mCNC film was also prepared with the drop-coating method with the toluene/mCNC suspension.
**Tensile Testing.** The tensile strength of all composite samples was investigated using uniaxial tensile testing on an Instron 5566 Universal testing machine. For the samples investigated in this work, the tensile strength occurred at the yield point. The samples were prepared by cutting the films with a dog bone die based on the ASTM D1708-13. The test section was approximately 22 mm long, 4.93 mm wide, and 0.6 mm thick. The testing speed was set as 1 mm/min. The ultimate tensile strength was taken as the maximum stress, and an average from at least five sample specimens was calculated for each composition.

**Gel Permeation Chromatography.** The molecular weight and polydispersity index (PDI) of PMMA and PMMA composites were measured using a Shimadzu gel permeation chromatography setup (GPC equipped with an RID-10A refractive index detector, an LC-20A chromatograph pump, and a CTO-20A column oven). DMF was used as the eluent at an operating temperature of 35 °C and a flow rate of 1 mL/min. Two 5 mm phenogel 10 E4A columns (molecular weight range: 200–2 × 10^5 g/mol) were calibrated using linear polystyrene (PS) standards.

**Scanning Electron Microscopy.** Composite samples were freeze-fractured with liquid nitrogen. The cryofracture surface was examined with a Zeiss Ultra-60 FE-SEM to reveal the surface morphology and CNC fractionation. Fractured composite films were mounted on sample holders with the fracture surface facing upward. The samples were then sputter-coated with Au/Pd in a Hummer sputtering system to prevent charge buildup during measurement. All images were obtained under an accelerating voltage of 5.0 kV.

**Polarized Light Microscopy.** CNC dispersion in the PMMA matrix was investigated qualitatively with an optical microscope (Olympus BXS1) equipped with two polarizers (Olympus U-AN360P). Large CNC aggregates will be observed as birefringence due to the crystallinity. Images were captured with an Olympus camera (U-CMAD3) and processed with PictureFrame software. All images were taken in a transmission mode with a 20X objective and at full extinction of the polarizer.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04246.

XPS, DSC, SEM images of cryofracture surfaces, photographs of samples, and GPC results (PDF)

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### REFERENCES

(1) Ranby, B. G.; Rübi, E. Ultrastructure of cellulose. Experien 1950, 6, 12–14.

(2) Moon, R. J.; Martini, A.; Naim, J.; Simonsen, J.; Youngblood, J. Cellulose nanomaterials review: structure, properties and nano-composites. Chem. Soc. Rev. 2011, 40, 3941–3994.

(3) Habibi, Y.; Lucia, L. A.; Rojas, O. J. Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications. Chem. Rev. 2010, 110, 3479–3500.

(4) Eyley, S.; Thielemans, W. Surface modification of cellulose nanocrystals. Nanoscale 2014, 6, 7764–7779.

(5) Habibi, Y. Key advances in the chemical modification of nanocelluloses. Chem. Soc. Rev. 2014, 43, 1519–1542.

(6) Giroud, N. M.; Xu, S.; Schueman, G. T.; Shofer, M. L.; Meredith, J. C. Site-Selective Modification of Cellulose Nanocrystals with Isophorone Diisocyanate and Formation of Polyurethane-CNC Composites. ACS Appl. Mater. Interfaces 2016, 8, 1458–1467.

(7) Xu, S.; Giroud, N.; Schueman, G.; Shofer, M. L.; Meredith, J. C. Mechanical and thermal properties of waterborne epoxy composites containing cellulose nanocrystals. Polymer 2013, 54, 6589–6598.

(8) Zhang, Y.; Karimkhani, V.; Makowski, B. T.; Samarayake, G.; Rowan, S. J. Nanomulsions and Nanolatexes Stabilized by Hydrophobically Functionalized Cellulose Nanocrystals. Macromolecules 2017, 50, 6032–6042.

(9) Kang, H.; Liu, R.; Huang, Y. Graft modification of cellulose: Methods, properties and applications. Polymer 2015, 70, A1–A16.

(10) Roman, M.; Dong, S.; Hirani, A.; Lee, Y. W. Cellulose Nanocrystals for Drug Delivery. In Polysaccharide Materials: Performance by Design; American Chemical Society, 2009; Vol. 1017, pp 81–91.

(11) Yan, W.; Chen, C.; Wang, L.; Zhang, D.; Li, A.-J.; Yao, Z.; Shi, L.-Y. Facile and green synthesis of cellulose nanocrystal-supported gold nanoparticles with superior catalytic activity. Carbohydr. Polym. 2016, 140, 66–73.

(12) Yalcinkaya, E. E.; Puglia, D.; Fortunati, E.; Bertoglio, F.; Bruni, G.; Vissai, L.; Kenny, J. M. Cellulose nanocrystals as templates for cetyltrimethylammonium bromide mediated synthesis of Ag nanoparticles and their novel use in PLA films. Carbohydr. Polym. 2017, 157, 1557–1567.
(13) Ali, U.; Abd Karim, K. J. B.; Buang, N. A. A. Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). Polym. Rev. 2015, 55, 678–705.

(14) Tan, Y.; Liu, Y.; Chen, W.; Liu, Y.; Wang, Q.; Li, J.; Yu, H. Homogeneous Dispersion of Cellulose Nanofibers in Waterborne Acrylic Coatings with Improved Properties and Unreduced Transparency. ACS Sustainable Chem. Eng. 2016, 4, 3766–3772.

(15) Xu, X.; He, L.; Zhu, B.; Li, J.; Li, J. Advances in polymeric materials for dental applications. Polym. Chem. 2017, 8, 807–823.

(16) Kedzior, S. A.; Graham, L.; Moore, C.; Dooley, B. M.; Cranston, E. D. Poly(methyl methacrylate)-grafted cellulose nanocrystals: One-step synthesis, nanocomposite preparation, and characterization. Can. J. Chem. Eng. 2016, 94, 811–822.

(17) Erbas Kiziltas, E.; Kiziltas, A.; Pollin, S. C.; Gardner, D. J. Preparation and characterization of transparent PMMA–cellulose-based nanocomposites. Carbohydr. Polym. 2015, 127, 381–389.

(18) Anzlovar, A.; Huskic, M.; Zagar, E. Modification of nanocrystalline cellulose for application as a reinforcing nanofiller in PMMA composites. Cellulose 2016, 23, 505–518.

(19) Sain, S.; Ray, D.; Mukhopadhyay, A. Improved mechanical and moisture resistance property of of in situ polymerized transparent PMMA/Cellulose composites. Polym. Compos. 2015, 36, 1748–1758.

(20) Banerjee, M.; Sain, S.; Mukhopadhyay, A.; Sengupta, S.; Kar, T.; Ray, D. Surface treatment of cellulose fibers with methacrylated for enhanced properties of in situ polymerized PMMA/ cellulose composites. J. Appl. Polym. Sci. 2014, 131, No. 39808.

(21) Hatton, F. L.; Kedzior, S. A.; Cranston, E. D.; Carlmark, A. Grafting-from cellulose nanocrystals via photoinduced Cu-mediated reversible-deactivation radical polymerization. Carbohydr. Polym. 2017, 157, 1033–1040.

(22) Abitbol, T.; Marway, H.; Cranston, E. D. Surface modification of cellulose nanocrystals with cetyltrimethylammonium bromide. Nord. Pulp Pap. Res. J. 2014, 29, 46–57.

(23) Hu, Z.; Berry, R. M.; Pelton, R.; Cranston, E. D. One-Pot Water-Based Hydrophobic Surface Modification of Cellulose Nanocrystals Using Plant Polyphenols. ACS Sustainable Chem. Eng. 2017, 5, 5018–5026.

(24) Ben Mabrouk, A.; Kaddami, H.; Magnin, A.; Belgacem, M. N.; Dufresne, A.; Boufi, S. Preparation of nanocomposite dispersions based on cellulose whiskers and acrylic copolymer by miniemulsion polymerization: Effect of the silane content. Polym. Eng. Sci. 2011, 51, 62–70.

(25) Tan, Y.; Liu, Y.; Chen, W.; Liu, Y.; Wang, Q.; Li, J.; Yu, H. Homogeneous Dispersion of Cellulose Nanofibers in Waterborne Acrylic Coatings with Improved Properties and Unreduced Transparency. ACS Sustainable Chem. Eng. 2016, 4, 3766–3772.

(26) Morandi, G.; Heath, L.; Thielemans, W. Cellulose Nanocrystals Grafted with Polystyrene Chains through Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP). Langmuir 2009, 25, 8280–8286.

(27) Morits, M.; McKee, J. R.; Majoinen, J.; Malho, J.-M.; Houbenov, N.; Seitsonen, J.; Laine, J.; Groschel, A. H.; Ikkala, O. Polymer Brushes on Cellulose Nanofibers: Modification, SI-ATRP, and Unexpected Degradation Processes. ACS Sustainable Chem. Eng. 2017, 5, 7642–7650.

(28) Habibi, Y.; Dufresne, A. Highly Filled Bionanocomposites from Functionalized Polysaccharide Nanocrystals. Biomacromolecules 2008, 9, 1974–1980.

(29) Siqueira, G.; Bras, J.; Dufresne, A. New Process of Chemical Grafting of Cellulose Nanoparticles with a Long Chain Isocyanate. Langmuir 2010, 26, 402–411.

(30) Cui, J.; del Campo, A. Multivalent H-bonds for self-healing hydrogels. Chem. Commun. 2012, 48, 931–933.

(31) Capitani, D.; Porro, P.; Segre, A. L. High field NMR analysis of the degree of substitution in carboxymethyl cellulose sodium salt. Carbohydr. Polym. 2000, 42, 283–286.

(32) Wu, X.; Moon, R. J.; Martini, A. Crystalline cellulose elastic modulus predicted by atomistic models of uniform deformation and nanoscale indentation. Cellulose 2013, 20, 43–55.

(33) Shang, W.; Huang, J.; Luo, H.; Chang, P. R.; Feng, J.; Xie, G. Hydrophobic modification of cellulose nanocrystal via covalently grafting of castor oil. Cellulose 2013, 20, 179–190.

(34) Biyani, M. V.; Foster, E. J.; Weder, C. Light-Healable Supramolecular Nanocomposites Based on Modified Cellulose Nanocrystals. ACS Macro Lett. 2013, 2, 236–240.

(35) Kargardazeh, H.; Sheltani, R. M.; Ahmad, I.; Abdullah, I.; Dufresne, A. Cellulose nanocrystal: A promising toughening agent for unsaturated polyester nanocomposite. Polymer 2015, 56, 346–357.

(36) Abraham, E.; Kam, D.; Nevo, Y.; Slattegard, R.; Rivkin, A.; Lapidot, S.; Shoseyov, O. Highly Modified Cellulose Nanocrystals and Formation of Epoxy-Nanocrystalline Cellulose (CNC) Nanocomposites. ACS Appl. Mater. Interfaces 2016, 8, 28086–28095.

(37) Segal, L.; Creeley, J. J.; Martin, A. E., Jr.; Conrad, C. M. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. Text. Res. J. 1959, 29, 786–794.

(38) Volpe, C. D.; Brugnara, M.; Maniglio, D.; Siboni, S.; Wangdu, T. About the possibility of experimentally measuring an equilibrium contact angle and its theoretical and practical consequences. In Contact Angle, Wettability and Adhesion, Vol. 4; Mittal, K. L., Ed.; CRC Press: London, 2006; pp 79–99.

(39) Beck-Candanedo, S.; Roman, M.; Gray, D. G. Effect of Reaction Conditions on the Properties and Behavior of Wood Cellulose Nanocrystal Suspensions. Biomacromolecules 2005, 6, 1048–1054.