PREPARATION OF CELLULOSE NANOCRYSTAL-POLYPROPYLENE MASTERBATCHES BY WATER-ASSISTED THERMOKINETIC MIXING

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Abstract

In an effort to avoid freeze-drying or solvent blending techniques and to better leverage the fact that preparation of cellulose nanocrystals (CNCs) result in aqueous dispersions, we investigated a water-assisted melt compounding approach to disperse cellulose nanocrystals in polypropylene (PP). A simple, water-based cetyltrimethylammonium bromide (CTAB) treatment of CNCs was used to reduce their hydrophilicity and inhibit hydrogen bonding. The aqueous suspension of treated CNCs was then blended with polypropylene in a thermokinetic mixer with various levels of a maleated polypropylene (MAPP) as a dispersing agent. CNC dispersion was evaluated by optical microscopy, scanning electron microscopy, and rheology. CTAB treatment alone was insufficient to provide good dispersion but dispersion improved greatly with increasing MAPP content. At the highest levels of MAPP, agglomerates were still present but nearly all were well below 1 µm in size. However, despite a CNC content of 8%, little rheological evidence of a network structure was found that would suggest well-dispersed nanocomposites.

Introduction

Cellulose nanomaterials represent a new class of cellulose-based material that can be extracted from trees, plants, some marine creatures such as tunicates, and certain bacteria or algae [1]. These materials are being investigated in a wide variety of applications and offer a number of potential advantages. For example, wood-derived cellulose nanomaterials are projected to be less expensive than many other nanomaterials and have the potential to be produced in large volumes [2]. They also have an impressive strength-to-weight ratio and have so far shown few environmental, health, and safety concerns in their unmodified state [2]. They are not a single material type but a family of materials with very different characteristics, largely due to differences in preparation methodology and source.

One type of cellulose nanomaterial that offers potential in polymer composites are cellulose nanocrystals (CNCs). CNCs, also called cellulose whiskers, nanowhiskers, or nanorods, can be produced by acid hydrolysis of cellulose pulps, for example. This results in high modulus, rod-like structures with aspect ratios of around 10-100 but whose dimensions and properties ultimately depend on the source of the cellulose and the exact preparation conditions. Plant-based sources typically yield crystallites with diameters of about 5 nm and lengths of about 100's of nanometers [3]. Figure 1 shows a transmission electron microscopy (TEM) image of CNCs derived from wood.

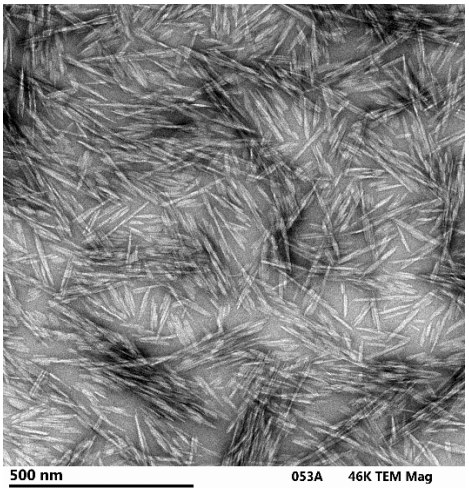

Figure 1. Transmission electron microscopy (TEM) image of wood-derived CNCs.

A number of potential composite applications require dispersion of the cellulose nanomaterials such as CNCs in a plastic matrix. However, there are challenges in doing so. For example, the preparation of CNCs results in aqueous dispersions while most plastics are hydrophobic. Additionally, CNCs have a strong tendency to hydrogen bond as they dry, making them difficult to disperse, particularly in hydrophobic matrices. Overcoming these challenges requires a strategic, holistic approach to water removal, simple and effective CNC treatments and/or targeted use of additives, and efficient processing.

There have been variety of approaches to rendering CNCs more hydrophobic [3]. However, many involve organic solvents, complicated/expensive chemistries, or large amounts of surfactant. One simple, water-based treatment that has been explored by some is treatment with cetyltrimethylammonium bromide (CTAB) [4, 5]. CTAB has a hydrophobic tail and an ammonium ion that can ionically bond with the negatively charged sulfate groups on the CNC surface that are produced during CNC preparation. Besides rendering the CNC more hydrophobic, hydrogen bonding is inhibited after treatment, which is why it has been used as a "debonding agent" in paper manufacturing. Also, CTAB treatment may facilitate some initial water removal since the CTAB-treated CNCs (CTA-CNCs) tends to settle out of its well dispersed state in water as it becomes more hydrophobic.

However, despite its positive effects, CTAB treatment alone is insufficient to allow it to be dispersed into common, hydrophobic matrices such as polyethylene or polypropylene (PP), at least not without further treatment, freeze drying, or additive technology. In an approach that is somewhat analogous to that used with nanoclays, we have initially investigated the addition of maleated polypropylene (MAPP) during compounding as a dispersing/coupling agent for CTA-CNCs. MAPP can potentially covalently bond with the hydroxyls of the CTA-CNCs.

In much of the literature on CNC composites in hydrophobic matrices such as PP, composites are often prepared by methods involving solvent-exchanging, solvent-blending, and film casting [6]. However, these are not the most commercially relevant approaches. The preparation of CNCs results in a water dispersion. Even after treatment, the more hydrophobic CNC still contains much water and traditional approaches have often involved freeze drying or spray drying to remove water but, hopefully, still allow it to be dispersed in plastics. However, these are slow processes and often aren't effective for incorporating CNCs in hydrophobic plastics unless the CNCs are very dilute or special techniques are used [7].

Supercritical or even subcritical fluids (e.g., nitrogen or carbon dioxide) have been used to facilitate the dispersion of nanoparticles during melt compounding [8, 9]. Extensional flows, created as the polymer rapidly foams due to fluid desolubilization, impart greater forces on polymer agglomerates than in shear, which predominates in conventional processing [9]. Water, either alone, in a nanoparticle slurry, or with a modifier such as a surfactant, has also been used to improve the dispersion of nanomaterials during melt compounding [10-12]. It is perhaps not surprising then that water-assisted compounding has been investigated for cellulose nanocomposite preparation since the starting material is a well-dispersed aqueous CNC suspension [6, 13]. This approach also has the added benefit of potentially eliminating a drying step.

We have recently had some success in improving CNC dispersion in polyamide 6 [14] and poly(lactic acid) matrices [15], for example, with a water-assisted compounding approach using a thermokinetic mixer. The thermokinetic mixer is a high-intensity batch mixer that has the advantages of small batch sizes for exploratory investigations, and the potential for short batch times and rapid water removal to minimize hydrolysis. Here we summarize the findings of our recent investigation on incorporating CNC into a more hydrophobic matrix (i.e. polypropylene (PP)), by:

1) Using a simple, water-based CTAB treatment of CNCs to reduce their hydrophilicity and inhibit hydrogen bonding.
2) Using a MAPP as a dispersing agent and water-assisted thermokinetic mixing to prepare masterbatches.

Experimental

Materials

A polypropylene, homopolymer flake (Fortilene HB 9100, melt flow = 2.7g/10 min. at 250°C, Bamberger Polymers) was used as the matrix plastic. Three additives were used to stabilize the plastic: 0.2% tris(2,4-di-tert-butylphenyl) phosphite, 0.1% pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), and 0.1% zinc stearate. The MAPP used had 8-10% maleic anhydride and a molecular weight of 9,100. The MAPP and cetyltrimethylammonium bromide (CTAB) were obtained from Millipore Sigma.

CNC preparation and treatment

The CNCs were produced in the Forest Products Laboratory's nanocellulose pilot plant by sulfuric acid hydrolysis, which is described elsewhere [16]. For the CTAB treatment, the CTAB was first dissolved in warm water and then slowly added to a 1% aqueous CNC dispersion while stirring. The initial weight ratio of CNC:CTAB was approximately 10:1 on a dry basis. After reacting for 1 hr under agitation, excess CTAB as well as the sodium and bromium ion byproducts were removed by dialysis for 15 hrs using a crossflow ultrafiltration unit. After dialysis, the CTA-CNC dispersion was concentrated in the same ultrafiltration unit by shutting off the make-up water. Further concentrating was performed at 10,000 RPMS for 20 min in a laboratory centrifuge (Sorvall fixed rotor, Kendro Laboratory Products) resulting in a final concentration of 13% solids.

Masterbatch and composite preparation

PP masterbatches containing 0, 2, 4, 8, 12 or 16% MAPP and sufficient CTA-CNC dispersion to yield 8% CTA-CNC in the final composites were prepared in 50g batches (dry basis) in a 1 liter thermokinetic mixer (K Mixer, Synergistics, Inc.). The water from the dispersion resulted in a water content of about 50% by weight, which was flashed off in the thermokinetic mixer during compounding. For all blends, a rotor speed of 5500 RPMs (tip speed of about 37 m/s) was used, and the discharge temperature was set at 105°C, which was measured by an infrared sensor mounted flush with the inside of the mixing chamber. Despite the low discharge temperature setting, some slight melting was seen suggesting localized heating under the rotors and away from the infrared sensor. Batch times were approximately 1 minute. The

material was then cooled, milled, and oven dried at 105°C.

The compounds were molded using a microcompounder and microinjection molder (DSM Xplore system, DSM Research, Geleen, Netherlands). Microcompounder barrel temperatures were set at 180°C, 190, and 200°C and the screw speed was 100 RPMs. A nitrogen blanket was used to minimize oxidative degradation. The material was transferred to the microinjection molder and small square plaques (25mm x 25mm x 1.2mm) were molded at 200°C at 8 bars of pressure for 10 seconds. The mold temperature was 60°C. 25mm diameter circular specimens were then cut from the molded plaques.

Characterization Methods

Sulfur and nitrogen analysis were performed on the CNC and CTA-CNC by Galbraith Laboratories, Inc. [17, 18]. Optical micrographs were taken on a Leitz Wetzlar Orthoplan-POL microscope. For transmission electron microscopy (TEM), a few drops of a diluted CNC solution (0.5 wt% in water) were deposited on a TEM copper grid and dried. The sample were imaged using a Philips CM-100 TEM (Philips/FEI Corporation) at an accelerating voltage of 100 kV. Surfaces of cryogenically fractured tensile specimens were imaged using a scanning electron microscope (Model LEO 1530, JEOL) at an accelerating voltage of 3 kV after sputtering with a gold-palladium alloy.

Small amplitude oscillatory shear (SAOS) tests were performed on a TA ARES rheometer with parallel plate geometry (25 mm plate diameter) at 195°C and a gap of 1.5 mm. The samples were equilibrated for 10 min prior to conducting an angular frequency sweep within the linear viscoelastic region from 0.05-100 rad/s.

Discussion

The ion exchange reaction for the CTAB treatment is shown below.

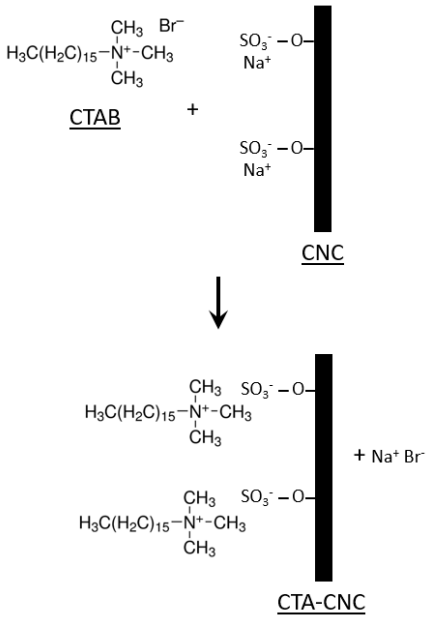

Figure 2. CTAB treatment of CNCs.

The chemical analyses of the CTA-CNC determined sulfur and nitrogen contents of 27 and 21 mmoles/g of CTA-CNC material, respectively. This indicates that only about ¾ of the sodium ions were exchanged with CTA ions. Others have recently shown that the relative CTAB and CNC concentrations as well as the reaction pH play a significant role in conversion efficiency of this reaction and that efficiencies near 100% are possible [4]. Therefore, there is potential to improve the efficiency of the reaction and increase the hydrophobicity and further inhibit hydrogen bonding of the CNC.

The effect of MAPP on the dispersion of CTA-CNC in the PP masterbatches was investigated by holding the CTA-CNC content constant at 8% and varying the amount of MAPP from 0-16%. Figure 3 shows optical micrographs of injection molded PP composites of the masterbatches at their original compositions except for the two masterbatches containing the highest MAPP contents (12 and 16%), which showed no obvious additional improvement in dispersion over the 8% MAPP masterbatch when examined under the microscope.

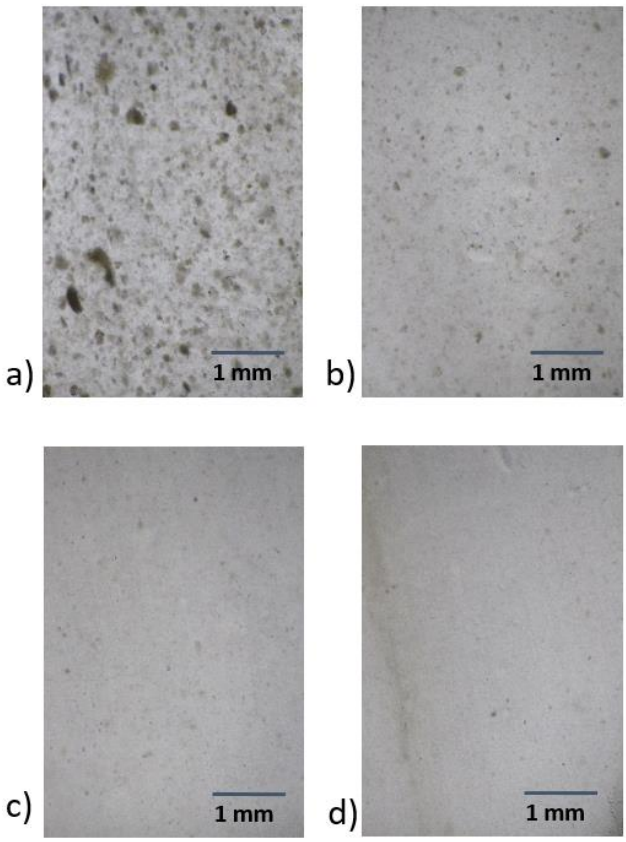

Figure 3. PP containing 8% CTA-CNC and a) 0%, b) 2%, c) 4%, and d) 8% MAPP.

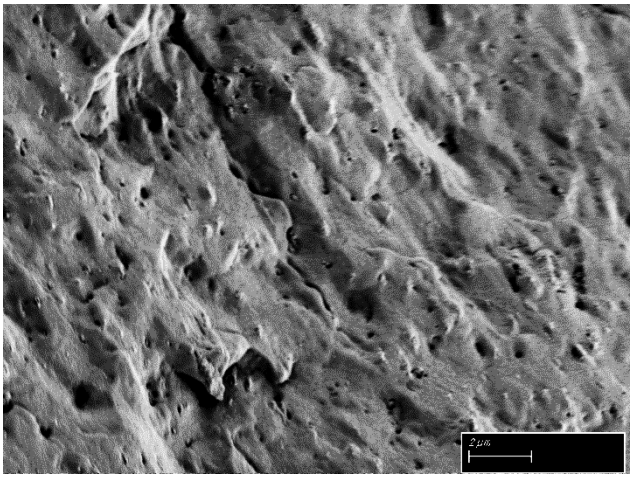

Figure 4. Scanning electron micrograph of a fracture surface of the composite of PP with 8% CTA-CNC and 16% MAPP) at high magnification. Scale bar is 2 microns.

Fig. 3 shows that the CTAB treatment alone is insufficient to yield well-dispersed composites and that dispersion is improved with MAPP content up to 8%. However, scanning electron microscopy showed that the dispersion was good but not optimal. For example, Fig. 4 is a scanning electron micrograph typical of the masterbatches with 8% or more MAPP. While few micron-scale agglomerates were found and the great majority of CNC material were well below micron size, they were certainly above the 5 nanometer diameter that would be expected for individual CNCs [1].

SAOS tests were conducted to investigate the rheological behavior of the masterbatches and further explore the dispersion of CNCs within them. The 8% CNCs added should be well above the percolation threshold if they are well-dispersed. A network would expect to be formed between the CNCs, possibly due, in part, to the maleated polypropylene and would be expected to influence the composite melt rheology. For example, Khoshkova and Kamal [7] found that a specialized, low concentration, spray freeze-drying method for CNCs led to well-dispersed composites that yielded: 1) a short linear viscoelastic region, 2) high resistance to flow at low frequency, and 3) both tan δ <1 and G' > G'' over a broad angular frequency range. Bagheriasl et al. [19] found significant effects in η^* and G' at low angular frequencies when freeze-dried CNCs and poly(ethylene-co-vinyl alcohol) were solvent-blended with PP but little effect when they were melt-blended in a twin screw extruder.

Figures 6 and 7 show the effect of MAPP content on the complex viscosity (η^*), storage modulus (G'), and loss modulus (G''). For brevity and clarity, the rheological behavior of only the composites that showed the best dispersion (i.e. 8-16% MAPP) is shown. Unfortunately, little effect of MAPP was seen on the melt rheology. No shifting of the curves nor plateauing at low angluar frequency was found in any of the curves that would indicate development of a network structure. This suggests that our approach has not yet yielded adequate dispersion to develop such a network structure and that further development is required.

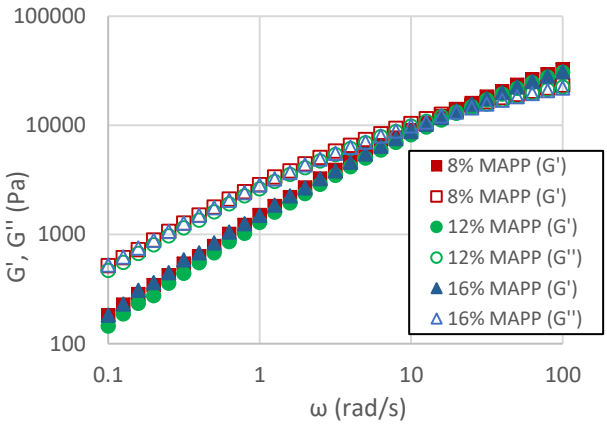

Figure 6: Effect of MAPP contents on storage modulus (G', solid markers) and loss modulus (G'', open markers).

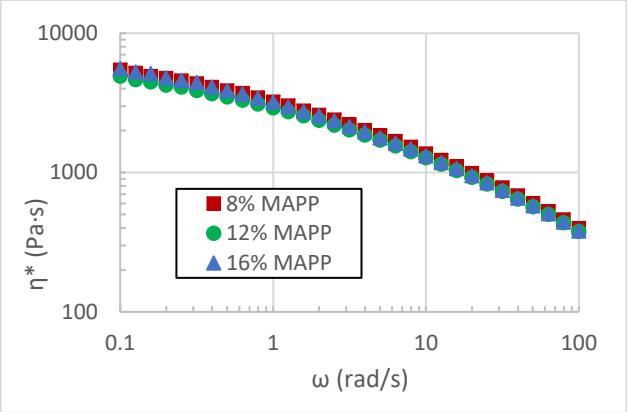

Figure 7. Effect of MAPP content on complex viscosity (η*).

Conclusions and Future Work

Initial experiments using a water-assisted thermokinetic mixing approach appeared promising for melt compounding of modified CNCs into PP provided that sufficient MAPP was added. Investigation by microscopy at several scales suggested good, though not perfect, dispersion. However, little rheological evidence was found for network formation, which would suggest a well-dispersed nanocomposite. Further exploration of the approach (e.g., optimization of CNC treatment, additives, and processing parameters) is warranted.

Acknowledgements

The authors would like to acknowledge the USDA National Institute of Food and Agriculture and the US Endowment for Forestry and Communities for partial funding of this research. We would also like to acknowledge Debby Sherman of DSimaging LLC for the TEM image of the CNCs as well as Phil Walsh of the Forest Products Laboratory for the scanning electron microscope imaging.

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