



Processing strategies for cellulose nanocrystal/polyethylene-co-vinyl alcohol composites



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ABSTRACT

Cellulose nanocrystals (CNCs) have garnered significant attention due in part to the remarkable properties of crystalline cellulose displayed at the nanoscale coupled with its availability from renewable resources. However, challenges exist in dispersing CNCs in thermoplastic polymers and assessing CNC dispersion. The purpose of this research was to investigate the impact different processing protocols had on CNC dispersion in two polyethylene-co-vinyl alcohol (EVOH) matrices and the resulting microstructure of the nanocomposites. Three processing strategies were proposed: a melt processing technique, a solution casting technique, and a combination of solution casting followed by melt processing. Polarized optical microscopy images of the nanocomposites showed that improved CNC dispersion and changes to the nanocomposite microstructure were observed when the multi-step protocol was implemented. Additionally, changes in microstructure as a function of comonomer ratios of EVOH suggested CNC dispersion changed as a result of differences in polymer-particle compatibility.

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1. Introduction

Cellulose nanocrystals (CNCs) have seen increased use as fillers in polymer nanocomposites due to their abundance, renewable source material, biodegradability, and potential mechanical properties [1]. In particular, high modulus and increased strength are expected due to the molecular structure in the nanoparticle and are attributed to the repeating ringed glucose units of cellulose as well as hydroxyl groups giving rise to a rigid crystalline structure with strong intermolecular bonding. Therefore, CNCs are promising candidates as mechanical reinforcement in polymer matrices. However, there are several challenges that persist as barriers to widely using CNCs in polymer composite applications. The hydrophilic nature of CNCs is generally incompatible with the hydrophobic nature of many commercial polymers. Additionally, CNCs have been reported to have degradation temperatures that fall below the processing temperature threshold of many common thermoplastic polymers. The degradation temperature for CNCs is approximately 200 °C [2,3], and many commercially important thermoplastic polymers are processed above this temperature.

CNCs have been incorporated into thermoplastic polymers with low melting temperatures via traditional melt processing methods found in industrial polymer processes, such as extrusion [4–7], compounding [4,8,9], and injection molding [10], and these approaches have produced composites with improved properties. Mariano et al. [7] reported the tensile modulus of CNC-reinforced polybutylene adipate-co-terephthalate (PBAT) increased compared to the neat PBAT when the nanocomposites were formed by melt extrusion with a twin screw extruder. They suggested the increased tensile modulus was as a result of the increased crystallinity of the polymer matrix when CNCs were introduced. Zhang et al. [10] reported polyvinyl alcohol (PVA) nanocomposites reinforced with CNCs via a multistep processing protocol including solution blending, melt mixing, and injection molding saw an increase in both tensile strength and tensile modulus with 7 wt% loading of CNCs. Groups attempting to incorporate unmodified CNCs (that is, CNCs that have not been further modified after sulfuric acid hydrolysis) report some discoloration of the nanocomposite or degradation of the CNCs [5,11,12]. One of the more heavily researched polymer matrices is polylactic acid (PLA) since it is also sourced from bio-based precursors [5,13–15] and expected to be reasonably compatible with CNCs. Oksman et al. [5] were able to incorporate CNCs derived from microcrystalline cellulose by pumping them in suspension in a PLA melt during extrusion.

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Discoloration of the nanocomposites after melt extrusion was attributed to the thermal degradation of CNCs after passing through the extruder set to a temperature of 180 °C. Despite some degradation being reported, they were still able to report significant increases in mechanical properties of the polymer matrix with 5 wt% CNC loading. To circumvent CNC degradation during melt processing, many reports indicate either the CNC surface chemistry or the polymer matrix was modified prior to incorporating and dispersing them in a polymer matrix via melt mixing [6,16–19]. Pereda et al. [19] were able to incorporate CNCs in a polyethylene matrix by first adsorbing polyethylene oxide chains to the surface of CNCs in order to increase the compatibility between the moieties. Qualitatively, the addition of PEO chains showed a reduction in discoloration and aggregation of CNCs in a polyethylene matrix when they were added and dispersed via melt extrusion. While Pereda et al. reported an increase in optical transparency of the nanocomposite films, they only observed a slight increase in the mechanical properties of the CNC-reinforced polyethylene nanocomposite.

Given the challenges associated with using conventional melt processing, much of the research about processing CNC-reinforced thermoplastic polymer matrix composites has employed solution processing methods [12,20,21]. Solution processing circumvents the thermal stability issues that can arise in polymer melt processes. Typical solution processing methods reported in literature include electrospinning [22–24], solution casting [12,25], gel spinning [26], and solution precipitation [11]. Significant increases in thermomechanical properties can be achieved in polymer matrices reinforced with loadings of less than 20 wt% of plant-based CNCs when they are processed by solution casting [27,28]. Peresin et al. [29] also reported a significant increase in storage modulus of PVA when CNCs were incorporated by electrospinning fibers. The authors attributed the increased mechanical reinforcement of PVA by the CNCs to an increase in hydrogen bonding between nanoparticles and the hydroxyl side groups of the polymer chains. Tensile modulus and strength of gel spun polyacrylonitrile (PAN) fibers were reported to increase by as much as 35% and 17%, respectively, when CNCs were incorporated into the fibers as reported by Chang et al. [30]. PAN chain alignment in the fiber axis and crystallinity were increased because of the incorporation and dispersion of CNCs by gel spinning in an organic solvent.

The choice of processing strategy plays an important role in CNC dispersion in thermoplastic polymers and presents a challenge to scalable production of CNC-reinforced polymer nanocomposites in industry. Additionally, characterizing CNC dispersion and distribution in a polymer matrix is either primarily qualitative or expensive to perform on a regular basis for quality control in industry. Efforts to map CNC dispersion with Raman spectroscopy may provide a characterization method to address this gap [31,32]. The purpose of this research was to more completely understand the efficacy of processing protocols to produce CNC/thermoplastic polymer composites with desirable mechanical properties as well as characterize CNC dispersion and distribution as a function of processing variables. As part of this work, processing-structure relationships were investigated. Single and multi-step protocols were investigated to determine what processing variables affect the ability of CNCs to disperse in a commercially available thermoplastic matrix, polyethylene-co-vinyl alcohol (EVOH). EVOH copolymers with two different comonomer contents were used and processed into composites using melt and/or solution processing methods.

Among polymers which could be good candidates for use with CNCs in composite applications, EVOH is an interesting choice since it should have some compatibility with CNCs through the vinyl alcohol component and this compatibility may be tunable by

changing the amounts of ethylene and vinyl alcohol content. Additionally, it is interesting from a practical perspective since it is primarily used in packaging applications due to its high oxygen and solvent barrier properties under dry conditions [33]. The comonomer content—measured as mole percent of each comonomer—dictates the thermal, mechanical, and barrier properties of the copolymer [34]. Generally, high vinyl alcohol content produces higher thermal, mechanical, and barrier properties for EVOH while higher ethylene content EVOH leads to a more readily melt-processable polymer formulation. Several formulations are reported to have processing temperatures that fall below the reported onset of thermal degradation of sulfuric acid hydrolyzed CNCs, namely with ethylene contents above about 40 mol% [34]. The reports found in literature that do investigate incorporating and dispersing CNCs in an EVOH matrix by Martínez-Sanz et al. used a combination of solution and melt mixing methods [11,35]. Those studies used a 32 mol% ethylene content EVOH copolymer (32EVOH) and incorporated sulfuric acid hydrolyzed CNCs derived from bacteria as well as wood fiber via solution and/or melt compounding methods. They observed that a multistep processing protocol was more effective in dispersing and distributing the CNCs. In this work, other types of EVOH polymers were explored as matrices for CNC composites, and building on this previous work, the CNC dispersion and distribution achieved following the individual processing steps were examined. Specifically, EVOH polymers with higher ethylene content (i.e. lower melting temperatures) were used to examine the effect of component compatibility and processing protocol on composite microstructure more fully.

2. Materials and methods

CNC/EVOH composites were processed using three different strategies and characterized to more fully understand the processing-structure relationships of these materials. CNCs were received in freeze-dried form from the USDA U.S. Forest Service Forest Products Laboratory (Madison, WI). These CNCs were derived from dissolving pulp and formed by hydrolyzing cellulose with 64% sulfuric acid followed by separation of the insoluble CNCs from the soluble byproducts via dilution, settling, and filtration [1,36]. For all three processing strategies, an aqueous suspension of CNCs was used. The process used for redispersing freeze-dried CNCs was derived from the process reported by Meree et al. [37]. Freeze-dried CNCs were suspended in deionized water and stirred with a Talboys overhead mixer model 134-1 at 1900 RPM for 90 min with a 5 cm diameter stainless steel propeller blade at room temperature in a fume hood. The final solids concentration of the CNC suspension was 5.5 wt%. Two EVOH polymers with different comonomer contents were used in this work. EVAL G156B, a 48 mol % ethylene content EVOH (48EVOH) was provided by Kuraray America, Inc. (Houston, TX). A 44 mol% ethylene content EVOH (44EVOH) was purchased from Scientific Polymer Products (Ontario, NY). Low density polyethylene (LDPE) was purchased from Sigma-Aldrich (St. Louis, MO). >99% isopropyl alcohol (IPA) (VWR) and distilled water were used in the solution processing methods.

As mentioned above, three processing strategies were employed to incorporate and disperse CNCs in EVOH: melt mixing via extrusion (melt), solution casting (solution), and solution casting followed by melt mixing (solution-then-melt, or STM). A HAAKE MiniLab Rheomix (Thermo Scientific) mini compounder with conical co-rotating twin screws and a Carver hot press were used for the melt and STM strategies. In the melt method, 48EVOH was investigated due to the melting temperature being the lowest of the two EVOH polymers. The first step was to purge the mini

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