



Cellulose nanocrystal/polyolefin biocomposites prepared by solid-state shear pulverization: Superior dispersion leading to synergistic property enhancements



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ABSTRACT

Cellulose nanocrystals (CNCs), a class of renewable bionanomaterials with excellent mechanical properties, have gained major interest as filler for polymers. However, challenges associated with effective CNC dispersion have hindered the production of composites with desired property enhancements. Here, composites of polypropylene (PP) and low density polyethylene (LDPE) with 5–10 wt% unmodified CNC are produced for the first time via a solventless process. In particular, we employ solid-state shear pulverization (SSSP). Optical and electron microscopy reveals excellent CNC dispersion with strongly suppressed degradation relative to composites made by melt mixing. Effective dispersion leads to major increases in Young's modulus, including a 69% increase in 90/10 wt% LDPE/CNC composites relative to neat LDPE, the highest modulus enhancement ever reported for polyolefin/CNC composites. The composites also exhibit superior creep performance with modest increment in yield strength compared to neat polymer. The LDPE/CNC composites retain elongation at break values that are equal to that of neat polymer while a decrease is observed with PP/CNC composites. The CNC thermal degradation temperature in air is close to that of PP melt processing conditions. We hypothesize that during melt-processing CNCs undergo preferential thermo-oxidative degradation in LDPE and simultaneous degradation in PP. Thus, CNC incorporation results in impaired thermal stability in LDPE and, especially, PP. Care must be taken in selecting the post-SSSP melt processing temperature and residence time in order to suppress degradation. Taking that into account, this study has produced polyolefin/CNC composites with superior dispersion and property enhancements and shown that CNC is an attractive filler for green polymer biocomposites.

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1. Introduction

In comparison to composites with micron-scale fillers (e.g., glass, carbon black, mineral fillers, etc. [1–7]), polymer nanocomposites exhibit property enhancements at much lower filler loadings and thus have gained widespread interest. Ever since the pioneering work two decades ago on polymer/layered silicate composites by Toyota researchers [8], a wide range of nanofillers

such as carbon nanotubes, expanded graphite, graphene, silica and calcium carbonate have been investigated in depth [9–25]. In addition, growing interest in developing a greener polymer industry has prompted researchers to explore green polymer composites [26], leading to the emergence of studies incorporating lignocellulosic materials such as rice husk, natural fiber and sawdust as fillers for plastics [27–35]. Detailed reviews of work on green polymer composites can be found in Refs. [36–39]. Besides cellulose-based natural fillers, several studies of composites with pure forms of cellulose such as microcrystalline cellulose have also been reported in depth [40–42]. In the current study, we investigate the potential of using cellulose nanocrystals as green nanofillers for the preparation of synergistic polymer composites.

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1.1. Brief background on cellulose nanocrystals and strategies for producing polymer composites

Individual cellulose crystallites known as cellulose nanocrystals that form the building blocks for cellulose structures in plants have attracted major interest recently as a green nanoreinforcing agent in polymer matrix composites (PMCs). The existence of such nanocrystallites was demonstrated as early as the 1950's [43,44]. Although such nanocrystals are known by several names such as nanofibrils, nanocellulose, and nanowhiskers, the Textile Association of Pulp and Paper Industry has proposed cellulose nanocrystals (CNCs) as the standard nomenclature. Cellulose nanocrystals can be conveniently extracted from bulk cellulose by mechanical or chemical treatment to separate out the crystalline phases. Commonly employed techniques include acid hydrolysis [45,46], TEMPO-mediated oxidation [47,48], and homogenization and grinding [49,50]. In addition to biorenewability, the extracted CNCs possess attractive properties including high modulus on par with Kevlar™ [51–53], uniform prismatic dimensions [51–53], low coefficient of thermal expansion [54], lyotropic liquid crystallinity [51–53], easy orientability under shear [54,55], refractive index on par with most polymers [56], high piezoelectric constants [57] and large surface area (~100 m²/g [51–53]). Pilot-scale plants for the production of CNCs are already operational with capacities up to 25 kg/batch [58,59]. It is estimated that the annual world-wide production of CNCs will increase by up to 500% by 2017, providing an abundant supply for the production of composites [53]. Large-scale production of CNCs is expected to reduce their overall cost, making them less costly than other nanomaterials like carbon nanotubes [60]. These attractive traits make CNCs highly desirable fillers.

The first efforts to produce PMCs with CNC date to the 1990s [61]. However, achieving homogenous dispersion of CNC in the host polymer matrix has been a major challenge. The hydrophilic nature of CNC and the large interfacial attraction due to its nanoscale dimensions result in significant filler agglomeration during processing, thereby dramatically impairing the ability of CNCs to act as nanoscale reinforcements for polymers [51–53,62,63]. Common strategies used to produce PMCs with CNCs are described in the following paragraphs.

A commonly employed strategy involves producing a stable colloidal dispersion of CNC in aqueous media. The presence of pendant sulfate groups left from acid hydrolysis steps during CNC production aids the formation of such dispersions. As a result, several studies have employed water-soluble polymers or polymer latex for making such composites [51–53,62–64]. Favier et al. [61] demonstrated for the first time the incorporation of CNC through emulsion polymerization with styrene/butadiene rubber. Composites of water-soluble polymers such as poly(vinyl alcohol) and poly(ethylene oxide) (PEO) have shown improvements in mechanical and barrier properties [65–67]. Recent studies have also produced water-based epoxy, elastomeric nanocomposites, and hydrogels incorporating CNCs [68–71].

Other studies have produced PMCs by employing surfactant-modified CNC to achieve good dispersion in aprotic solvents such as toluene [72–74]. However, relatively few studies have attempted to produce composites of polyolefins with cellulose nanocrystals due to solubility limitations. Ljungberg et al. [75] employed pristine and surfactant-modified cellulose whiskers in hot toluene to produce solvent-cast composite films with polypropylene (PP). Such composites with 6 wt% unmodified cellulosic whiskers showed impaired mechanical properties with brittle fracture and elongation values that were only 50% of strain at yield of neat PP. Agarwal et al. [76] dissolved maleic anhydride-grafted PP/CNC mixtures in toluene. Upon solvent evaporation, the resulting powder was

milled and blended in a lab-scale extruder into filaments. Because of poor dispersion, the modulus of the PP composite with 2 wt% CNC was only 17% higher than that of neat PP. Bahar et al. [77] employed ultrasonication to disperse pristine cellulose nanowhiskers in toluene. This dispersion was then used to produce composites with neat PP employing maleic anhydride-grafted PP (MAPP) as compatibilizer under strong magnetic stirring. Such composites with 10 wt% cellulose nanowhisker and 2 wt% MAPP exhibited a 20% reduction in Young's modulus with respect to neat PP. Besides resulting in ineffective dispersion, such solvent-based techniques are unlikely to be adopted commercially because they are both expensive and environmentally unfriendly.

Relatively few studies have produced polyolefin/CNC composites by industrial processing techniques such as melt extrusion. The inability of melt mixing to provide sufficiently large shear stresses to break up and disperse CNCs results in large CNC agglomerates within the polymer [53]. Moreover, the presence of sulfate groups in CNCs leads to inferior thermal stability with degradation temperatures close to 150 °C [78,79]. Thus, attempts at achieving filler dispersion in polyolefins via melt extrusion, which employs long mixing times, and high temperature (~200 °C for PP and poly(lactic acid) (PLA)) is often accompanied by major filler degradation [79–82]. Studies have investigated different strategies to prevent CNC degradation. For instance, end-group functionalized CNC with organic acid chloride [82] or CNC grafted with poly(caprolactone) [80], poly(vinyl alcohol) [83], or PLA [81] have been extruded with polyolefins. Cellulose nanocrystals wrapped with PEO or high molecular weight polyamides have also been used to produce composites via melt extrusion [84–88]. Recently, Oksman and co-workers have employed a liquid feeding technique for producing composites of PLA and a colloidal dispersion of CNC via melt extrusion [81,83].

To prevent CNC degradation, researchers have chosen low-melting-point polyolefins such as low density polyethylene (LDPE) as matrix polymers [82]. Dufresne and coworkers [82] produced composites with pristine CNC and CNC functionalized with long chain organic chlorides. Such LDPE/pristine CNC composites with 10 wt% filler exhibited 25 and 85% reductions in tensile strength and elongation at break, respectively, with only a 24% increase in Young's modulus. On the other hand, CNC functionalization impaired the modulus and tensile strength of the composites. In another study by Dufresne and coworkers [87], water soluble PEO was blended with equal masses of aqueous CNC dispersions, freeze dried, and then melt blended with LDPE. When 9 wt% 1.0×10^6 g/mol PEO-wrapped-CNC was incorporated into LDPE, the resulting composite exhibited a 60% increase in modulus and maintained the elongation to break value of neat LDPE [87]. All strategies discussed above involve either additional chemistry, which reduces the green aspect of the CNCs and adds cost, or employ hygroscopic compatibilizers or surfactants that add processing steps and cost. Thus, there is a need for a simple, industrially scalable, green strategy for producing polyolefin composites with well-dispersed CNCs.

1.2. Solid-state shear pulverization: A new strategy for producing polyolefin/CNC composite materials

Here, we employ a single-step, solventless, continuous and industrially scalable process called solid-state shear pulverization (SSSP) [14,15,19,89–103] to produce green composites of polyolefins and CNCs with excellent dispersion and remarkable property enhancements compared to those reported in literature. (The SSSP process is one of a class of solid-state processing methods including mechanical milling techniques such as ball and pan milling that have been used in studies of polymer composites and

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