



Water-assisted compounding of cellulose nanocrystals into polyamide 6 for use as a nucleating agent for microcellular foaming



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ABSTRACT

Cellulose nanocrystals (CNCs) are a biorenewable filler and can be an excellent nucleating agent for the development of microcellular foamed polymeric nanocomposites. However, their relatively low degradation temperature limits their use with engineering resins like polyamide 6 (PA6) in typical melt processing techniques such as injection molding, compounding, and extrusion. A water-assisted extrusion compounding process was investigated to directly compound CNC suspensions with PA6 without the need of predrying the CNCs. By using water as a plasticizer and reducing the processing temperature by 30 °C, this process can mitigate the degradation of CNCs during compounding. The effects of the CNCs on the mechanical properties, crystal type, and microstructure of solid and microcellular foamed specimens were characterized. The CNCs primarily acted as a nucleating filler, affecting both the matrix crystal structure and, in foamed composites, the cell structure. The CNCs nucleated the α -crystalline form of PA6 and also acted as a foam cell nucleator, increasing cell density by an order of magnitude while significantly reducing cell size. The weight reduction of the foamed specimens was about 15%. Adding small amounts of CNCs also increased matrix orientation in the solid injection molded specimens. These factors helped to improve the mechanical performance, especially the modulus of elasticity. During water-assisted compounding, thermal hydrolysis of PA6 occurred and generated carbon–carbon double bonds, as evaluated by FTIR. However, the molecular weight reduction caused by hydrolysis was less than 5%. The total molecular weight reduction was around 18%, combined with the melt extrusion and injection molding processes.

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1. Introduction

Microcellular injection molding, which employs a supercritical fluid (SCF; usually nitrogen or carbon dioxide) as a physical blowing agent, can fabricate lightweight, dimensionally stable plastic parts while using less material and energy [1–3]. The SCF is capable of plasticizing the polymer, as well as decreasing its melt viscosity and processing temperature. In the microcellular injection molding process, supercritical CO₂ or N₂ is accurately metered into the barrel

and quickly dissolves into the polymer melt to form a single-phase polymer/gas solution due to the high shear generated by the screw. Upon injection, the thermodynamic instability triggers homogeneous and/or heterogeneous cell nucleation, followed by cell growth that helps foamed parts to fill the entire mold cavity. Micro- and nano-fillers (e.g., nanoclay [4], talc [5,6]) are sometimes used as nucleating agents to refine and stabilize the cell structure, which can enhance the tensile strength and modulus, and even the toughness and impact strength, as a result of a synergistic effect of combining the microcellular process with nanofillers. Cellulose nanocrystals (CNCs) are a new class of biorenewable nanofillers that hold promise as a nucleating agent for micro-cellular injection molding.

CNCs are derived from native cellulose, an abundant polysaccharide that is the main structural component of trees, plants, and marine creatures like tunicates, certain bacteria, and algae [7].

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CNCs have great potential as biorenewable fillers for polymers due to their abundance in nature and their high mechanical performance. They are prepared by hydrolyzing amorphous cellulose with concentrated acid while leaving behind the crystalline portions. This results in a highly crystalline, high modulus fiber, which is not surprising given that the modulus of native cellulose I crystals is typically about 138 GPa [8]. The actual modulus of the CNCs depends on the source of the cellulose and the specifics of the extraction method. In addition to high mechanical performance, CNCs have been found to nucleate biodegradable polymers with relatively low melting temperatures like poly(ϵ -caprolactone) [9] through the microcellular foaming process.

However, the relatively low degradation temperature of CNCs (around 200 °C) limits their use in many thermoplastics, especially engineering resins, which are often prepared by melt processing near or above this temperature. Moreover, the preparation of CNCs results in aqueous gels or suspensions that cannot easily be incorporated into most polymers. Consequently, water soluble polymers such as polyvinyl alcohol [10–12] and polyethylene glycol [13] have been investigated as matrices for CNC composites [11]. However, this approach greatly limits the types of composites and applications where CNCs can be used. Various drying methods (e.g., freeze drying) have also been investigated, but dried CNCs are very difficult to uniformly disperse in polymeric matrices via melt compounding because blending shear stresses cannot completely break the inter-particle hydrogen bonds that are formed during drying.

An alternative approach to incorporating CNCs into polymers such as PA6 is by water-assisted compounding. In water-assisted compounding, filler suspensions are directly fed into an extruder and the water acts as a compatibilizer or surfactant carrier, for example, that can enhance filler dispersion. This approach has been used to exfoliate and disperse mineral fillers (e.g., montmorillonite nanoclay, halloysite nanotubes) in polymeric matrices such as polypropylene [14–17], PA6 [18,19], PA11 [20], and PA12 [21,22]. Additionally, the melting temperature of PA6 is sensitive to water [23–25] and can be lowered by approximately 60 °C if the water content is over 30 wt% and pressures are greater than 0.8 MPa [26,27]. This is known as the “cryoscopic effect” [19] and would lower the melting point sufficiently to mitigate degradation of the CNCs. Such an approach is particularly appropriate for CNCs since their preparation results in aqueous suspensions.

Polyamide 6 (PA6), also known as nylon 6, is an engineering thermoplastic polymer that is widely used in many applications such as molded parts, sheets, films, fibers, and cords. The primary chemical structure of polyamides contains amide groups which can form hydrogen bonds leading to high mechanical properties. However, the thermal stability and dispersion challenges of CNCs mentioned above have largely prevented the preparation of these types of composites except when using methods like solvent casting [28,29], which has limited practicality. The use of scalable water-assisted compounding of CNCs into PA6 is an opportunity to overcome these limitations.

Therefore, we investigated a novel method of high-pressure, water-assisted melt compounding to disperse biodegradable CNCs in PA6. Solid and microcellular injection molded PA6/CNC specimens were then produced from the compounded materials. The effects of CNCs on the mechanical properties, PA6 crystal structure, foaming behavior, and possible PA6 degradation were investigated.

2. Experimental work

2.1. Isolation of materials and CNCs

Polyamide 6 (PA6, Ultramid 8202, BASF) with a density of 1.13 g/cm³ was used as the polymeric matrix resin. CNCs were prepared at the U.S. Forest Service, Forest Products Laboratory (Madison, WI). Briefly, commercially available dissolving pulp dry lap made from southern pine was acid hydrolyzed by 64% sulfuric acid at 45 °C for approximately 1.5 h under a nitrogen blanket with constant stirring. The CNCs were neutralized by adding an aqueous sodium hydroxide solution of about 5% concentration. The sodium sulfate and other salts were removed by ultrafiltration in a tubular ultrafiltration unit. The final CNC suspension concentration was approximately 12.2 wt%. The aqueous CNC suspensions were diluted to various concentrations with deionized water and then microfluidized, resulting in solutions with final concentrations of 1.7, 6.5, and 11.0 wt%, as tabulated in Table 1. The density of solid CNCs was about 1.5 g/cm³.

2.2. Water-assisted compounding

A 32 mm DTex twin-screw extruder (Davis Standard, U.S.) was used to compound the CNCs into PA6. Fig. 1 shows a schematic of the water-assisted compounding process and screw element arrangement. PA6 commercial pellets melted at the first zone of the screw (that contained elements 1–9). The CNC suspension was metered into the center section of the barrel via a 260D cylinder pump (Teledyne ISCO, U.S.) aggressively compounded with the molten PA6. To ensure that the water remained liquid, the center section of the extruder barrel was pressurized to 1.8–2.1 MPa, as adjusted by injected nitrogen, which is different than using a standard twin-screw extruder configuration and compounding with low pressure. Reverse kneading elements and sealing rings were used as a melt seal to maintain the high pressure. The various concentrations and flow rates of the diluted CNC suspensions injected into the barrel are listed in Table 1. Flow rates were selected to provide water concentrations of about 28 wt% of the PA6 melt. Barrel temperatures were set at 220, 235, 235, 235, and 235 °C (from the hopper to the die) for typical PA6 melt compounding, and the processing temperatures were adjusted to 220, 235, 205, 205, 205, and 235 °C after the CNC suspensions were pumped into the extruder barrel in the middle zone where the temperature was 30 °C lower than that of a typical process. The water was vented at the last metering zone (elements: 30–36) and the resulting compound was then granulated. The PA6 compounds with 0.5, 2.0, and 3.5 wt% CNC concentrations were dried in a vacuum oven at 80 °C for 24 h before solid and microcellular injection molding.

2.3. Microcellular injection molding

Solid and foamed tensile test bars (ASTM D638, Type I) [30] were injection molded via a molding machine (Arburg Allrounder 320S, Germany) with commercial microcellular injection molding (MuCell) SCF injection units. The testing bars obtained a thickness of 3.2 mm. The processing temperatures were set at 214 °C for solid specimens and 204 °C for foamed specimens, and the mold temperature was 80 °C for both. The circumferential speed of the injection screw was 15 m/min and the injection speed was 60 cm³/s, leading to a very short melt mixing time in the barrel (less than 1 min). For the microcellular injection (foamed) molding processes, 2–3 wt% nitrogen was added as a blowing agent. The back pressures were 5.5 and 1.0 MPa for the foamed and solid specimens, respectively. The weight reduction of the foamed specimens was

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