

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.

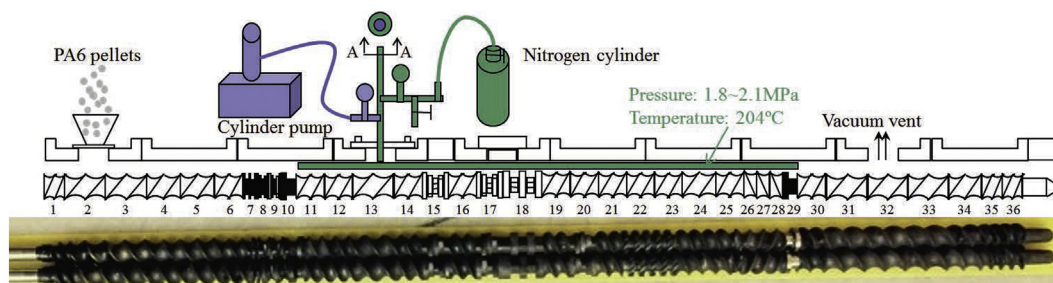
2.3. Microcellular injection molding

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

Table 1

Various concentrations and flow rates of diluted CNC suspensions metered into the twin-screw extruder barrel.

CNC concentration of solid PA6/CNCs (wt%)	Diluted CNC suspension (wt%)	CNC suspension flow rate (ml/min)	PA6 feeding rate (g/min)	Water concentration over PA6 (wt%)
0.5	1.7	22.0	75.6	28.7
2.0	6.5	23.0	75.6	28.8
3.5	11.0	23.8	75.6	28.5

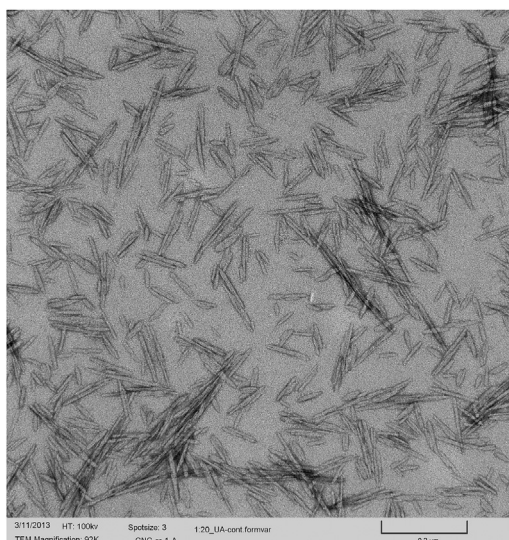
**Fig. 1.** Schematic of the water-assisted compounding process. The injection rate of CNC suspension was controlled by the cylinder pump, and the high pressure in the middle of the barrel was regulated by nitrogen.

13–15 wt% compared to their corresponding solid counterparts. Molded specimens with CNC concentrations of 0.5, 2.0, and 3.5 were denoted as nanocomposites NC0.5, NC2.0, and NC3.5, respectively, injection molded raw neat PA6 as NR (neat resin), and water-assisted compounded and then injection molded PA6 as NRW, which would have the same thermomechanical history as the injection molded nanocomposites.

2.4. Material characterization

2.4.1. Transmission electron microscopy (TEM)

The structure and dimensions of the CNCs were investigated by TEM. A few drops of the diluted CNC solution (0.5 wt% in water) were deposited on a TEM copper grid and dried. The sample grids were analyzed using a Philips CM-100 TEM (Philips/FEI Corporation, Holland) at an accelerating voltage of 100 kV. The morphology of the cellulose nanocrystals is shown in Fig. 2.

**Fig. 2.** TEM image of cellulose nanocrystals. The scale bar is 200 nm.

2.4.2. Scanning electron microscopy (SEM)

The surfaces of the cryogenically fractured specimens were analyzed using a scanning electron microscope (SEM; JEOL LEO 1530, Japan) at an accelerating voltage of 3 kV. The cell size and density of the foamed specimens along both the cross-sectional and flow directions were evaluated by ImageJ software developed by the National Institutes of Health (1.48d, U.S.).

2.4.3. Wide-angle X-ray diffraction (WAXD)

X-ray diffraction patterns were obtained with a D8 Discovery Diffractometer (Bruker Corporation, U.S.) by irradiating the neat and filled PA6 with Cu K α radiation. The accelerating voltage and current were 50 kV and 1 mA, respectively. PA6 crystal orientation was determined using the most intense equatorial diffraction arcs, those corresponding to the (200) planes of PA6. Herman's orientation parameter (f) was calculated to describe the crystal orientation, as defined by Equations (1) and (2) [31].

$$f = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \quad (1)$$

$$\langle \cos^2 \varphi \rangle = \frac{\sum_0^{\pi/2} I(\varphi) \sin \varphi \cos^2 \varphi}{\sum_0^{\pi/2} I(\varphi) \sin \varphi} \quad (2)$$

where φ is the azimuthal angle and $I(\varphi)$ is the intensity along the Debye–Scherrer ring. The value of f ranges from -0.5 to 1 for perfect orientation perpendicular to and parallel to the tensile bar flow direction, respectively. Random orientation yields a value of f of 0 .

2.4.4. Tensile testing

Tensile properties were evaluated using a tensile testing machine (Instron 5967, MA) with a 30 N load cell, a gauge length of 25.4 mm, and an extension rate of 10 mm/min according to ASTM D638 guidelines [30]. The experimental results were evaluated as an average of 7 measurements.

2.4.5. FTIR

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FTIR spectrometer at a resolution of 1 cm^{-1} in the

frequency range of 4000 cm^{-1} to 400 cm^{-1} . The analyses were performed on the surface of the solid and foamed bars at ambient temperature.

2.4.6. Viscosity average molecular weight

Each of the PA6 samples was diluted in formic acid (85%) to yield solution concentrations of 0.2, 0.4, 0.8, and 1.0 mg/ml. After equilibrating at $25\text{ }^{\circ}\text{C}$, 8 ml of the PA6 solution were poured into a Cannon–Fenske glass capillary viscometer. The flow times were determined and repeated three times. Only neat PA6 samples were measured since the nanoscale fillers of the CNCs could not be filtered out to eliminate their effects on the viscosity. The relative viscosities were analyzed by the Huggins and Kraemer equations [32] to determine the intrinsic viscosity and the viscosity average molecular weight estimated by means of the Mark–Houwink equation,

$$[\eta] = k \cdot (M_v)^a \quad (3)$$

where k and a are constants for the PA6–formic acid system [33,34].

3. Results and discussion

3.1. CNCs as a nucleating agent of foamed specimens

PA6/CNC nanocomposite compounds were first produced by water-assisted compounding. Next, solid and micro-cellular foamed specimens were injection molded. The dispersion of CNCs in the solid composites is shown in Fig. 3. Compared with the smooth surface of the cryogenically fractured pure NR (Fig. 3 (a)), CNC particles, highlighted by yellow circles, can be seen in the

cross-section of NC2.0 (Fig. 3 (b)). The aggressive melt processing (i.e., compound-ing and injection molding) may have broken the original needle-shaped CNC rods into CNC particles. Also, residual acid on the CNCs after production could conceivably stimulate further hydrolysis through water-assisted compounding under pressure. We found similar nanocellulose particles in our previous work on drawn filaments of polyvinyl alcohol/short cellulose nanofibrils.³⁵ ENREF_40 Short cellulose nanofibrils prior to processing had needle shapes comparable to the CNCs here. Souza also reported that needle-shaped chitosans were broken into particles by ultrasonication [36]. In addition, even though the majority of CNCs were well dispersed, occasional clusters were also found (cf. Fig. 3 (c); highlighted by a yellow circle).

To investigate the effect of CNCs as nucleating agents on the morphology of microcellular foamed PA6, cryogenically fractured surfaces were examined using scanning electron microscopy (SEM) along two directions: the melt flow direction and perpendicular to the melt flow (i.e., along the cross-section of the tensile bars). Fig. 4 shows the microstructure of the foamed specimens, and Fig. 5 indicates the average cell size and cell density transverse to the mold filling direction. Filled PA6 samples possessed smaller cells than those of neat PA6 along both the cross-section and flow directions.

According to classic nucleation theory [37,38], homogeneous nucleation occurs when gases dissolved in a polymer melt form a stable cell nucleus, whereas heterogeneous nucleation occurs at the interface between the polymer and the fillers because of surface energy differences. The homogeneous nucleation of foamed NR samples was triggered by a thermodynamic instability when the PA6/N₂ solution was injected into the cavities. Cell nucleation competes with cell growth for gas consumption during foaming. The relatively low homogeneous nucleation rate produced foamed

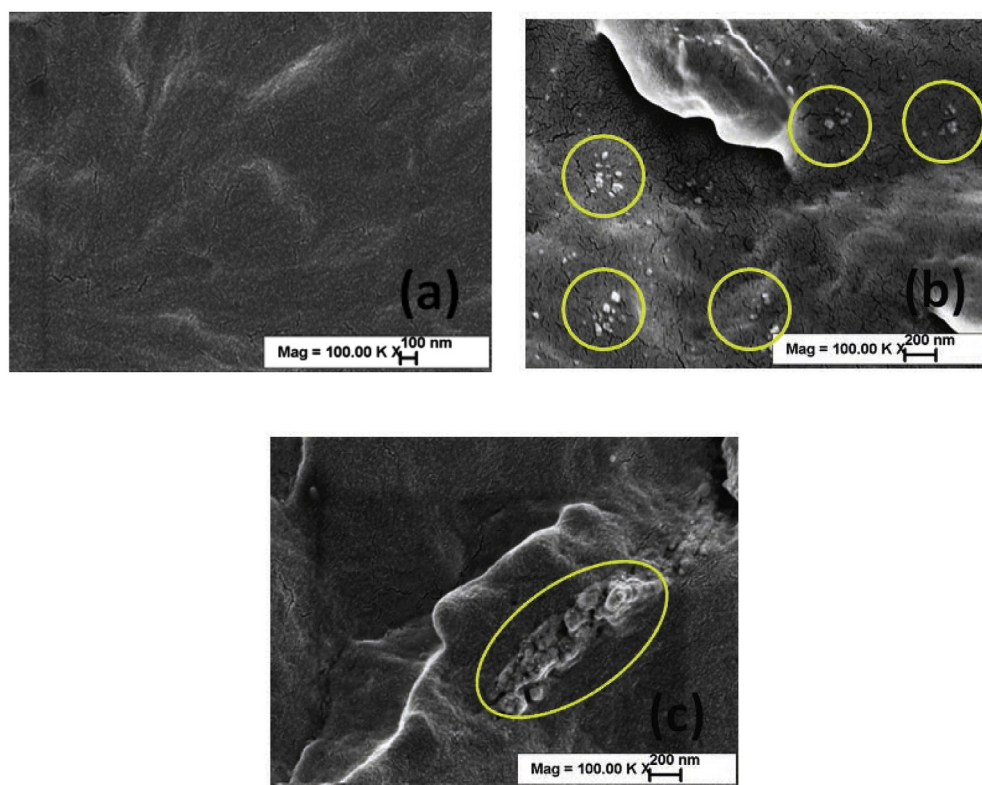


Fig. 3. SEM images of the cryogenic fracture surfaces along the cross-section showing (a) neat solid PA6, (b) CNCs dispersed in a PA6 matrix of a solid NC2.0, and (c) a CNC agglomerate in the solid NC3.5 specimens. The yellow circles highlight the CNCs and an agglomerate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

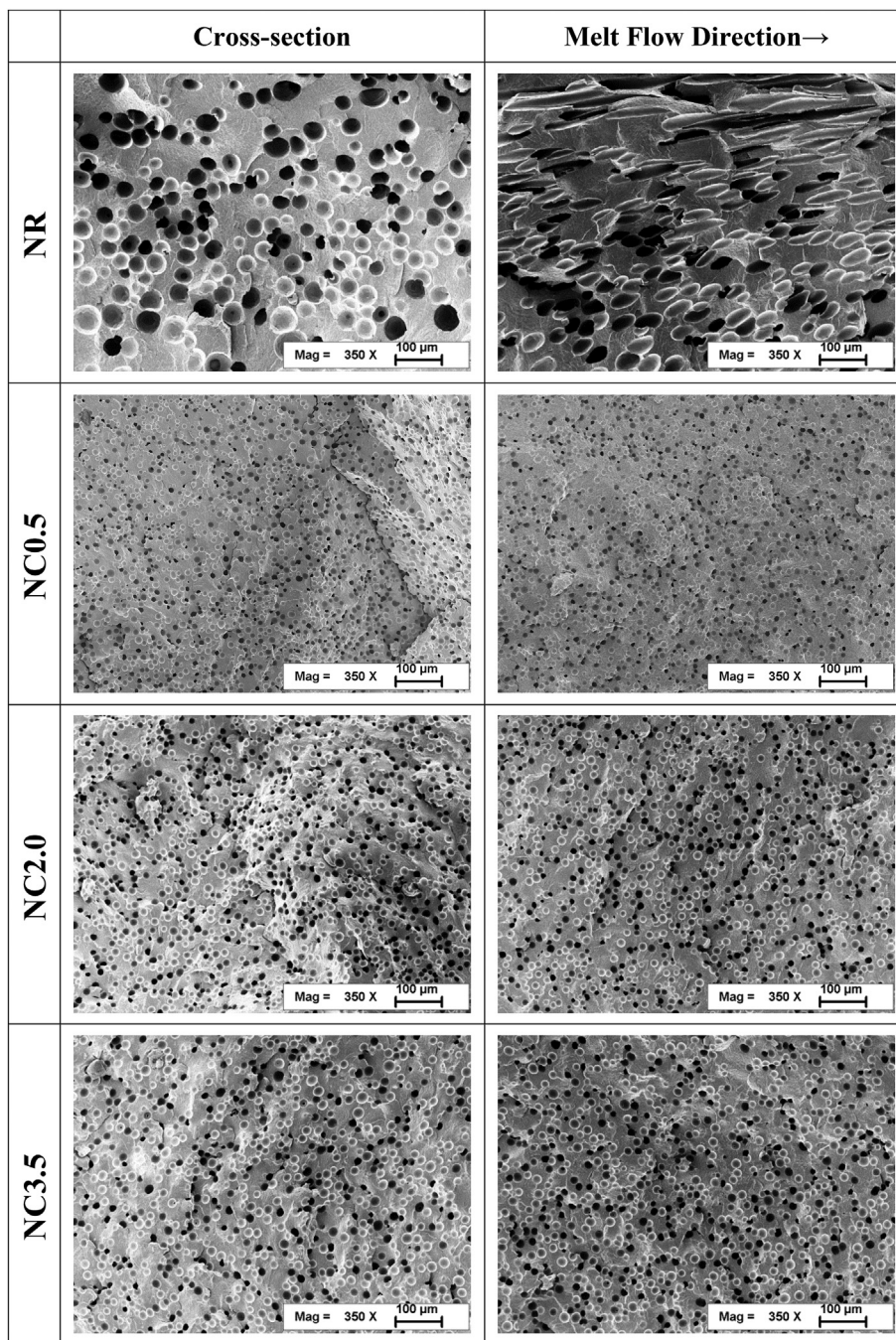


Fig. 4. SEM images of the fractured surfaces of foamed PA6 with various CNC concentrations as nucleating agents. Scale bars denote 100 μm .

NR with a cell density of $1.1 \times 10^7 \text{ cell/cm}^3$. As Fig. 4 shows, the cells in the middle layer were spherical, whereas those close to the skin layer of the foamed specimens were ellipsoidal as a result of the extensional flow due to the fountain-flow behavior at the advancing melt front, as well as the shear friction. The bubbles on the skin layer of the foamed NR samples were elongated along the melt flow direction by the friction generated by the relative cold mold wall during mold filling; some stretched voids collapsed and coalesced into orientated bubbles. Extensional and shear stresses may also have caused cell rupture as mold filling proceeded.

In comparison with neat foamed specimens, adding 0.5 wt% CNCs reduced the cell size and increased the uniformity by reducing the energy barrier for cell nucleation. The resulting higher

nucleating density yielded finer cell sizes and higher cell densities. With the addition of 0.5 wt% CNCs, the cell diameter was about $12 \mu\text{m}$ with a cell density of $1.3 \times 10^8 \text{ cell/cm}^3$. All of the cells of NC0.5 were uniform spheres, even near the skin layer. When the cells were small enough, the extensional or shear forces generated by the flow and mold friction could not rupture or elongate the cells due to their smaller surface areas in comparison with that of foamed NR cells. Adding more than 0.5 wt% CNCs yielded larger cells due to cell rupture and coalescence.

Moreover, cell growth can improve filler dispersion by biaxially stretching the cell wall. For example, Yuan et al. reported that, for nanoclay in PA6, cell growth stretched the polymer and nanoclay around the cell and the resulting elongational flow improved

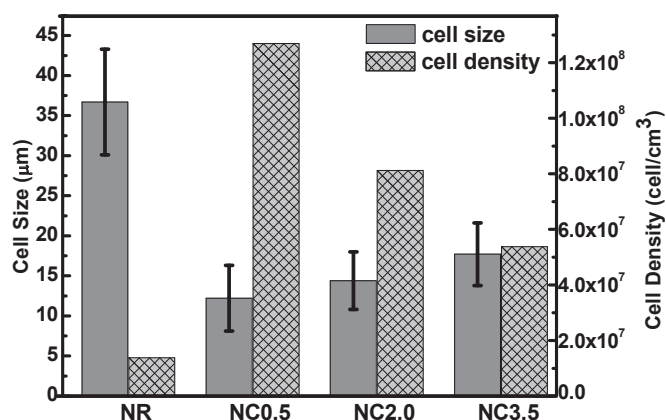


Fig. 5. Representative values of the average cell size and cell density of foamed PA6 samples along the cross-section direction based on SEM images.

their solid counterparts. In general, adding CNCs increased the Young's modulus. These tensile properties would be expected to depend on the polymeric matrix (i.e., molecular chain orientation and crystal structure) and the filler (i.e., dispersion and concentration), as well as the foam cell structure. In the following sections, various characterization techniques were used to explore these effects on tensile performance.

Recall that in our water-assisted compounding approach, aqueous CNC suspensions were injected into the pressurized extruder barrel to minimize CNCs' degradation and improve their dispersion in the PA6 matrix. However, the incorporation of water during compounding can also potentially affect PA6 itself. Two-dimensional wide angle X-ray diffraction (2D WAXD) was used to probe the possible changes in crystallinity and crystal structure of the PA6. Solid NR specimens had only one relatively broad crystalline peak at $2\theta \sim 21^\circ$, which was attributed to the (200) planes of the monoclinic (γ) form (Fig. 8). However, the water-assisted

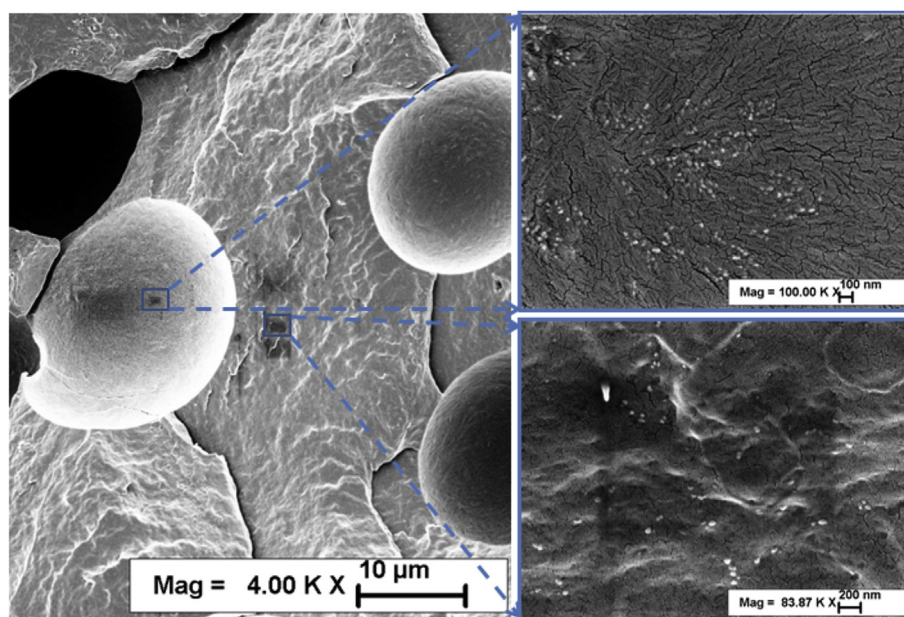


Fig. 6. SEM images of the cryogenic fracture surfaces of a foamed NC3.5 specimens along its cross-section. CNCs dispersed on the foam cell wall (upper right) as nucleating agents and in the bulk PA6 matrix. The scale bars denote 100 nm in the upper right image and 200 nm in the lower right image.

nanoclay dispersion [4]. Fig. 6 shows some dispersed CNCs as cell nucleating agents on the cell wall, and some in the polymeric matrix. Several uniformly dispersed CNCs were found on a single void wall, suggesting that more than one CNC particle nucleated a single cell or that the cells coalesced (see Fig. 6).

3.2. Tensile properties

The mechanical properties of the solid and foamed injection molded specimens are shown in Fig. 7. NRW specimens, compounded via water-assisted compounding, had higher Young's moduli than NR specimens. The reason for this interesting behavior will be discussed below. Solid specimens had higher Young's moduli and ultimate strengths than their foamed counterparts. Conceivably, the cells within the foamed specimens reduced the effective cross-sectional area and thus affected the Young's modulus and ultimate strength. Nonetheless, if one takes into account the weight reduction, then the specific Young's modulus and the tensile strength of the foamed specimens will be comparable to

compounded specimens (NRW) showed a shoulder at $2\theta \sim 23^\circ$, which was attributed to the (002 + 202) planes of the monoclinic (α) form [28,39]. The α -form crystallized when the chains were in the fully extended zigzag conformation and the hydrogen-bonded sheets were antiparallel to each other, while the hydrogen-bonded sheets were parallel in the γ -form. The γ -form had a shorter chain axis dimension causing a torsion of chains due to a tilting of the amide group [40,41]. The Young's modulus of the α -form was found to be higher than that of the γ -form [41]. This increase in the α -form by water-assisted compounding helped explain the increase in modulus of NRW versus NR. Even with drying prior to injection molding, the granulated PA6 via water-assisted compounding conceivably possessed more bound water than the conventionally compounded alternative. Murthy [23] reported that annealing under water or ethylene glycol resulted in similar PA6 crystal transformations. As Fig. 8 (a) shows, adding CNCs also increased the α (002 + 202) peak intensity, thus suggesting that CNCs acted as crystal nucleating agents for the α -form.

Moreover, the solid PA6 tensile properties also depended on

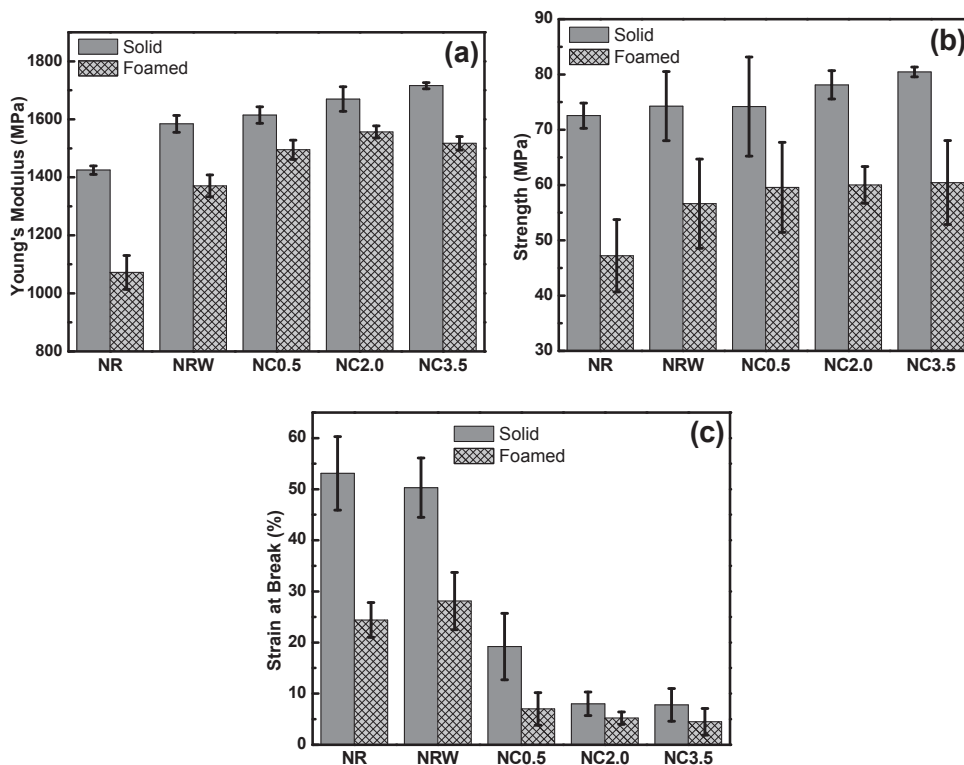


Fig. 7. Tensile properties of solid and foamed specimens: (a) Young's modulus, (b) ultimate strength, and (c) strain at break.

chain extension and molecular orientation, which was largely affected by the addition of CNCs. Due to low CNC filler concentrations, the diffraction patterns of the CNCs themselves could not be discerned. Concentric halos in the X-ray diffraction pattern in Fig. 8 indicated random PA6 crystal orientations; whereas equatorial arcs from the (200) planes of the PA6 crystals suggested some alignment along the flow direction. Table 2 summarizes the Herman's orientation parameter (f) calculated from the (200) planes. In the solid specimens, the crystal orientation increased with the addition of 0.5% CNCs, possibly due to a lubricating effect of the tightly bound water in the CNCs or even themselves increasing their molecular mobility and alignment during mold filling. Our previous work showed that short cellulose nanofibrils could improve matrix molecular chain orientation during hot drawing of polyvinyl alcohol fiber [35]. After an increase in PA6 crystal orientation with 0.5% CNCs, any further addition decreased orientation (Table 2), possibly as a result of the beginning of CNC percolation and network formation [42]. This partial network formation could hinder chain mobility and, consequently, PA6 crystal orientation. Therefore, the improved Young's moduli of solid filled PA6 nanocomposites likely resulted from enhanced PA6 molecular orientation and induced crystal structure transformation as well as filler concentration.

As for the foamed specimens, the cell microstructure (i.e., cell size and density) were critical factors in the tensile properties. More uniform cell sizes and high cell densities were found to retain the Young's moduli. As shown in Fig. 7 (a), foamed PA6 with CNCs had higher tensile moduli than solid NR samples, even at a weight reduction of 13–15%. This was probably because of the finer cells created by heterogeneous nucleation (Figs. 4 and 5) and the filler and crystal nucleating effects of the CNCs. A similar trend has been found for other PA6 nano-composites. For example, Yuan reported that fine, uniform cell structures improved the storage moduli of PA6–nanoclay composites [4]. In addition, the moduli of

microcellular injection molded composites exhibited similar trends as solid specimens with CNCs nucleating the higher modulus α -crystal structure, as shown in Fig. 8 (b) and Table 2. However, the trends in PA6 crystal orientation with the addition of CNCs in solid specimens were not found in the foamed composites (Table 2), probably due to the combined effects of plasticizing SCF and foaming behavior during microcellular injection molding.

Little reinforcement from CNCs, in terms of increased tensile strength, was found for either the solid or foamed specimens (Fig. 7 (b)), likely because of the low aspect ratio of the CNCs. What improvements were found were likely due to the increased PA6 molecular orientation in the solid specimens [43] or a finer and more uniform cell structure in the foamed ones. The strain-at-break values were adversely affected by the addition of CNCs, and foamed cells served as stress concentrators. Previous work showed similar results regarding the negative effects of nano-cellulose as a reinforcement, even though the fillers possessed strong adhesion with the matrix, since rigid reinforcements typically have a lower strain-at-break [11,35]. The voids of the foamed parts decreased the effective cross-sectional area, and further decreased the elasticity in comparison with their neat solid semi-crystalline counterparts. [1].

3.3. PA6 degradation

Water and high temperature can potentially cause thermal or hydrolytic degradation of PA6. To investigate the decomposition caused by the high-pressure water-assisted compounding process, a Cannon–Fenske routine viscometer was employed to determine the average molecular weight reduction, and Fourier transform infrared spectrometry (FTIR) was used to characterize chemical changes that might be associated with degradation.

The viscosity average molecular weight was determined to examine the effects of thermal and hydrolytic degradation during

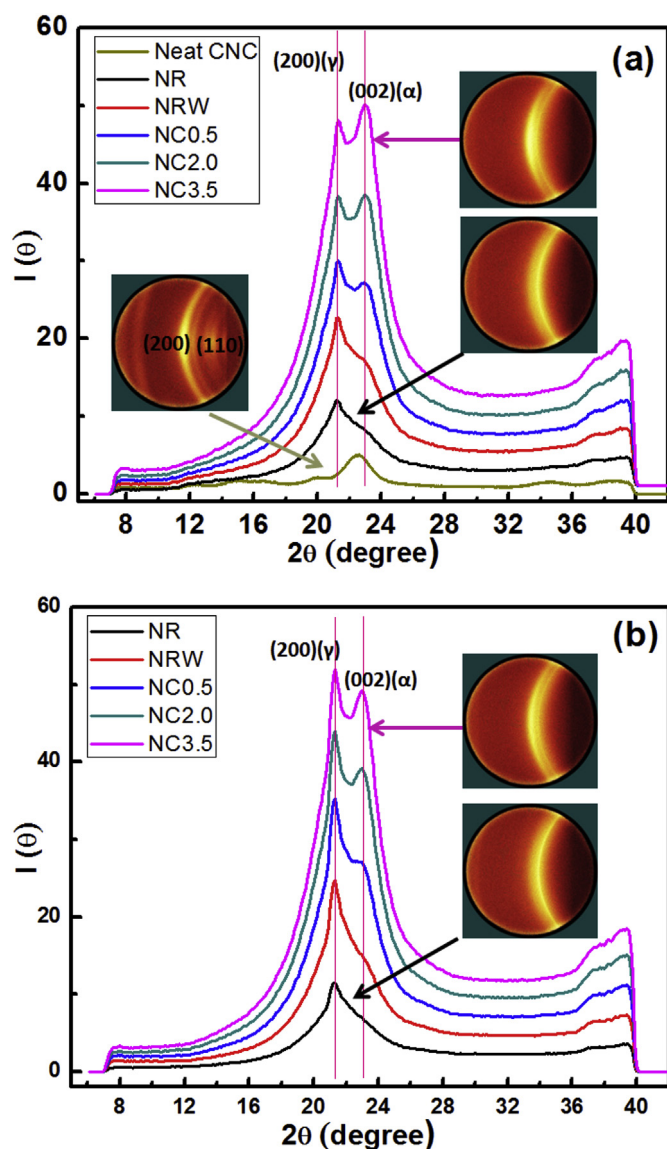


Fig. 8. WAXD patterns of pure CNC cast film, injection molded (a) solid and (b) foamed neat PA6 and nanocomposites.

Table 2
Herman's orientation parameter (f) based on XRD measurements of PA6 nanocomposites.

Samples		Herman's Parameter (f_c)
Solid	NR	0.49
	NRW	0.47
	NC0.5	0.63
	NC2.0	0.56
	NC3.5	0.54
Foamed	NR	0.47
	NRW	0.46
	NC0.5	0.46
	NC2.0	0.43
	NC3.5	0.48

processing (cf. Table 3). Conventional extrusion compounding followed by injection molding reduced the molecular weight by 13.6% compared to the original commercial PA6 pellets, whereas the addition of water during the compounding step reduced it by 17.6% overall. However, the reductions in PA6 molecular weight caused

Table 3

The viscosity average molecular weight evaluation of solid PA6 via the compounding and injection molding process with and without water.

	Molecular weight	
	(g/mol)	Reduction (%)
Control PA6 pellets	28622	0.0
Extruded strand without water	25908	−9.5
Extruded strand with water	24903	−13.0
Injection molded solid NR	24738	−13.6
Injection molded solid NRW	23575	−17.6

by water via the water-assisted com-pounding seen here resulted in an additional loss of less than 5% compared to what was seen without adding water (13.0 versus 9.5%; 17.6 versus 13.6%).

Fig. 9 shows the FTIR spectra of the control commercial PA6 pellets that had not been extruded or processed, solid NRW and NC3.5 specimens, and pure CNC film. Solid NRW and NC3.5 specimens were produced via high-pressure water-assisted compounding and injection molding processes. Because of their low concentrations and peak overlap, the CNC characteristic peaks were not obvious in the spectra for the NC3.5 specimens. The band at $\sim 1640\text{ cm}^{-1}$ was attributed to the symmetrical bending of the NH group and stretching of the C=O double bond, and the FTIR spectra were normalized based on this peak.

The possible PA6 degradation pathway and products were dependent on the temperature and the presence of a nucleophile such as water [44]. Considering the availability of water and the processing temperature of 204°C during water-assisted compounding, hydrolytic scission of the amide bond is possible, leading to acid ends and amine end groups. Also, Fig. 9 shows a vinyl group ($\sim 970\text{ cm}^{-1}$) [45] in NRW and NC3.5, but the peak was not observed in commercial PA6 pellets. In addition, Davis [46] suggested that melt processing causes PA6 degradation in which olefin and ammonia are generated. The olefin produced during melt processing may explain the C=C double bond shown at 965 cm^{-1} . Therefore, degradation by both thermal processing (i.e., injection molding) and hydrolytic degradation with water as a nucleophile was possible during the processes used.

4. Conclusions

A water-assisted compounding approach was successfully used

to compound CNCs into polyamide 6, and expand the applications of CNCs as biorenewable fillers by melt processing. This technique directly used the aqueous CNCs' water suspension that resulted from its preparation without the requirement of pre-drying as in other approaches. By compounding the CNCs with the PA6 prior to

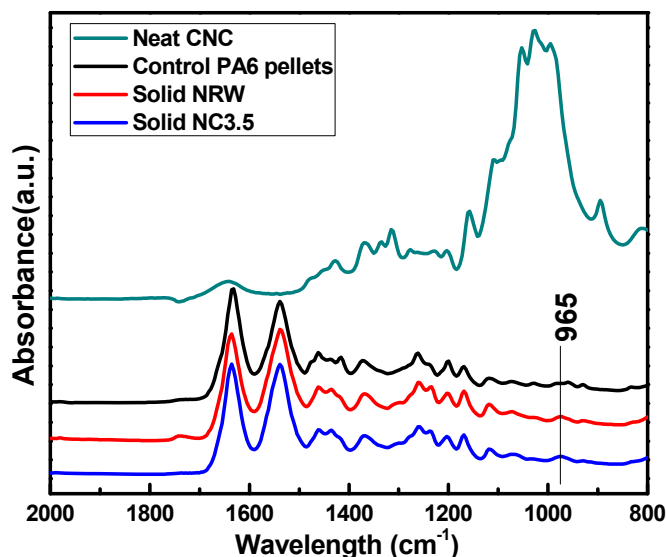


Fig. 9. Normalized FTIR spectra of 100% CNC cast film, commercial PA6 pellets, and solid injection molded NRW and NC3.5 specimens.

water removal, CNCs' agglomeration and hydrogen bonding caused by drying and consequent dispersion challenges were mitigated.

The CNCs primarily acted as a nucleating filler rather than a reinforcement, affecting both the matrix crystal structure and, in the foamed composites, the cell structure. The CNCs nucleated the α -crystalline form of PA6 and also acted as a foam cell nucleator during micro-cellular injection molding, increasing cell density by an order of magnitude and reducing cell size. Adding small amounts of CNCs also increased the matrix orientation in the solid injection molded specimens. These factors resulted from the addition of CNCs, and the foamed cells helped to improve the mechanical performance (i.e., Young's modulus and strength) of the solid and foamed parts, except for the strain-at-break. The weight reduction of foamed specimens was about 15%. FTIR spectroscopy showed an increase in unsaturation created by thermal hydrolysis during water-assisted compounding. However, while the overall molecular weight reduction was around 18%, that caused by hydrolysis appeared to be less than 5%.

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