JOURNAL OF Applied Polymer SCIENCE

# Nano-crystalline cellulose, chemical blowing agent, and mold temperature effect on morphological, physical/mechanical properties of polypropylene

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**ABSTRACT:** Polypropylene (PP)/nano-crystalline cellulose (NCC) composites and foams were produced through extrusion compounding combined with injection molding. From the samples produced, a complete morphological, physical, and mechanical analysis was performed to study the effect of NCC concentration (0–5wt %), foaming agent content (0 to 2wt %) and mold temperature (30°C and 80°C). NCC was very effective to reduce cell size (42–71%) and increase cell density (5–37 times) of the foams, while slightly increasing the overall density (2–7%). The results showed that NCC addition increased the specific tensile modulus (15–22%), specific tensile strength (1–14%) and specific flexural modulus (13–26%) of PP, but decreased specific impact strength (10–20%) and specific elongation at break (50–96%). © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42845.

**KEYWORDS:** cellulose and other wood products; composites; foams; mechanical properties; nanoparticles; nanowires and nanocrystals

Received 4 June 2015; accepted 17 August 2015
**DOI: 10.1002/app.42845**

## INTRODUCTION

Polymers reinforced with natural fibers have received increasing interest over the past decades because of advantages such as low cost, low density, high stiffness, ease of processing, $CO_2$ sequestration, and biodegradability.[1–6] Although several studies are still performed on fillers like clays,[7–12] calcium carbonate,[13,14] and carbon nanotube,[15–17] recent investigations focussed on natural fibers such as jute, hemp, flax, and sisal to improve the physical and mechanical properties of polymers.[18–21] These works used lignocellulosic fibers in thermoplastic materials to study the effect of processing methods and conditions, as well as coupling agent and fiber contents.[22–26] Among these studies, few of them used nano-crystalline cellulose (NCC) which is a rod-like, highly crystalline particle obtained from acid hydrolysis of cellulose. But in most of the works performed on NCC the samples were produced via solution casting because of challenging issues related to thermal stability and dispersion. Nevertheless, some efforts have been done to produce NCC filled thermoplastic composites via melt blending.[27–31] In our previous studies, the addition of 5wt % of NCC was shown to improve the tensile (23% in modulus and 10% in strength) and flexural (32% in modulus) properties of nylon 6 (PA6) nano-composites produced by extrusion coupled with injection molding.[32,33]

Although natural fibers are effective to reduce the overall composites density compared to synthetic or inorganic fillers, their lower impact strength and higher density than the neat resin are limiting their use. So, the idea to produce foams was proposed to solve these shortcomings. Foamed plastics sometimes could be stronger than their unfoamed counterparts, especially when specific properties are compared (weight basis). They can also give exceptional performance/cost ratio because of the lower amount of raw material needed.[34,35] Foams also have other advantages such as improved surface definition, sharper corner, and smoother surface.[3]

Several matrices like polystyrene, polypropylene (PP), polyethylene, and polyvinylchloride have been used to produce wood composite foams with a wide range of wood content and reduced density.[2] Among all the foaming processes (either batch or continuous), injection molding is the most important commercial process for a wide variety of polymers. But to get good foam structures, an optimization of the processing parameters, mostly mold temperature and cooling time, is needed.

As mentioned before, NCC is a potential reinforcement and nucleation agent to produce composite foams. In this work, a nonpolar matrix was used (PP) to compare the results with our previous work using a polar matrix (PA6). In particular, the effect of NCC concentration (0 to 5wt %), chemical foaming agent (CFA) content (0, 1, and 2wt %) and mold temperature (30 and 80°C) on the morphological, physical and mechanical properties are reported and discussed in terms of specific

properties; i.e. values divided by density. Overall, results showed that all three parameters had effect on the mechanical and morphological properties. Especially NCC in the range used was found to be very effective to reduce cell size and increase cell density of the foams, while slightly increasing the overall density. It also improved the specific tensile modulus, specific tensile strength, and specific flexural modulus of PP, but decreased specific impact strength and specific elongation at break of the samples produced.

## EXPERIMENTAL

### Material

PP (Formolene® 4101O, Formosa plastics corporation, USA) with a density of 0.90 g/cm$^3$ and a melting temperature of 160°C was used. The NCC (FPInnovations' NCC pilot plant, produced by acid hydrolysis of a commercial bleached softwood Kraft pulp) with a degradation temperature of 290°C and a crystallinity of around 78%,[36] was used as the filler. Activated azodicarbonamide (Celogen 754A, ChemPoint, USA) was applied as CFA. Its decomposition temperature range was 165–180°C and produced 200 cm$^3$ of gas per gram.

### Sample Preparation

Before blending, NCC was dried at 70°C for 24 h. For nanocomposites production, a Haake twin-screw extruder Rheomex PTW 16 OS ($L/D = 25$) with a die diameter of 3.2 mm was used. The flow rate was fixed at 0.5 kg/h and the temperature profile was set at 175°C, 185°C, 185°C, 185°C, 180°C, and 170°C from the feed zone to the die. To get good dispersion, a 5wt % NCC masterbatch in PP was first produced. Then, the masterbach was pelletized and diluted with virgin PP to produce NCC nano-composites with different NCC contents (0, 0.5, 1, 3, and 5wt %). Finally, all the samples were foamed using the CFA (dry-blended) at two different concentrations (1 and 2wt %) in a laboratory injection molding machine (Nissei PS60E9ASE, Japan). The injection temperature was set at 190°C and two different mold temperatures (TM) of 30°C and 80°C were used to see their effect on foam structures. The mold had four cavities producing samples for tensile, flexural, and impact tests according to ASTM D638, D790, and D6110, respectively.

### Characterizations

**Morphology.** A scanning electron microscope (SEM) JEOL JSM 840A was used to capture images at different magnifications from the broken surfaces of the samples that were first frozen in liquid nitrogen and then coated with Pd/Au. The micrographs were analyzed with Image-Pro Plus 4.5 software (Media Cybernetics, USA) to evaluate skin thickness, as well as cell diameter and cell density in the core. The reported values are the average and standard deviation of at least three different images giving a minimum of 100 cells. It is possible to obtain the average cell diameter directly by the Image-Pro software assuming that the cells are spherical and have isotropic distribution. For cell density ($N_f$), the number of cells ($n$) in an image (with correction for border cells) of surface $A$ in cm$^2$ gives:[37]

$$N_f = \frac{n}{A}\left(\frac{n}{A}\right)^{\frac{3}{2}} \quad (1)$$

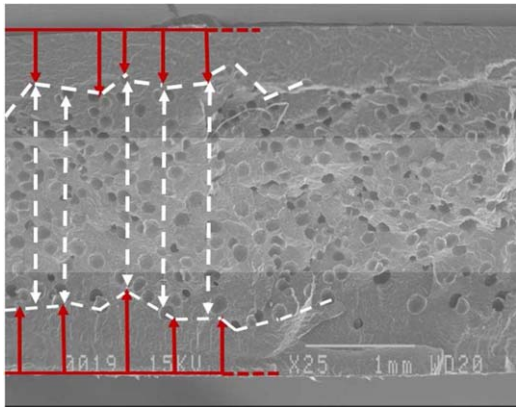


**Figure 1.** Typical morphology of a structural foam: two unfoamed skins (solid lines) enclosing a foamed core (dashed lines). Molding conditions: NCC = 3wt %, CFA = 1% and TM = 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the foam structure, lines were drawn perpendicular from the surface and the average of filled and dashed lines (see Figure 1) were reported as skin and core thicknesses, respectively.[21]

**Density.** Density measurements were done on a gas pycnometer (nitrogen) model Ultrapyc 1200e (Quantachrome Instruments, USA). Each value is the average of five tests.

**Tension.** The tensile properties were measured using an Instron model 5565 universal testing machine (Instron, USA) with a 500 N load cell. Dog bone shaped samples were directly produced by injection molding according to ASTM D638 (type IV). The tests were performed with a crosshead speed of 10 mm/min at room temperature. Reported values for Young's modulus, tensile strength, and elongation at break were based on the average of five samples.

As mentioned before, the mechanical properties of the foams were measured to determine the effect of NCC concentration, CFA content, and mold temperature. To do so, specific property ($P_S$) is defined as the ratio between the sample property ($P$) and its density ($\rho$) as

$$P_s = \frac{P}{\rho} \quad (2)$$

**Flexion.** Flexural tests were done on an Instron universal tester model 5565 with a 50 N load cell according to ASTM D790 with a crosshead speed of 2 mm/min at room temperature. Sample dimensions were 125 × 12.5 × 3.14 mm$^3$ and the span length was fixed at 60 mm. At least five samples were used to calculate the average and standard deviation.

**Impact.** Charpy impact strength test was performed on a Tinius Olsen (USA) testing machine model Impact 104 operating with a pendulum weight of 242 g (1.22 J). Rectangular samples (60 × 12.5 × 3.14 mm$^3$) with "V" notch produced by an automatic sample notcher model ASN (Dynisco, USA), at least 24 hours before the tests, were prepared according to ASTM D6110. All the tests were done at room temperature and the results are the average of at least five measurements.

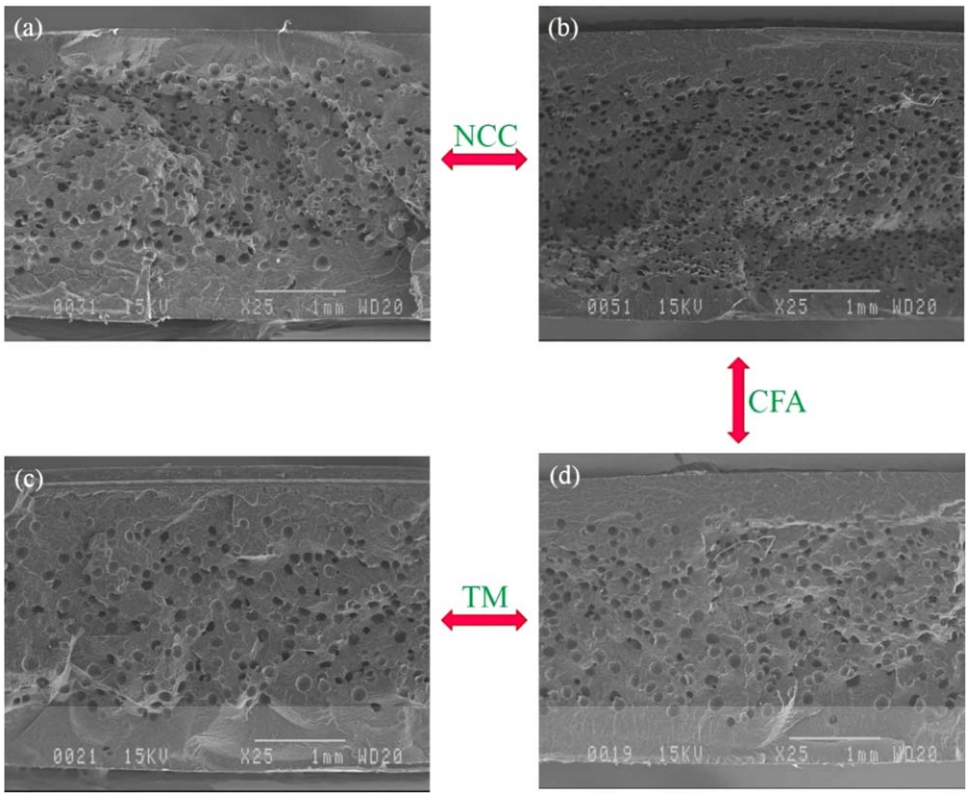


**Figure 2.** SEM images of PP foamed at 80°C and 2% CFA with different NCC contents: (a) 0 and (b) 3wt %, and samples with 1% CFA and 3wt % NCC at different mold temperatures: (c) 30°C and (d) 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## RESULTS AND DISCUSSION

### Morphology

Typical SEM images presented in Figure 2 can be used to determine the effect of the studied parameters (NCC and CFA contents, mold temperature) on foam morphology. Figure 2(a,b) show that for a fixed CFA content (2%) and mold temperature (80°C), increasing NCC content from 0 to 3wt % increased the number of cells and consequently decrease their sizes because of NCC nucleation effect.[38] Comparing Figure 2(b,d) (fixed NCC content of 3% and mold temperature of 80°C), increasing the CFA content from 1% to 2% clearly increased the cell density and decreased the average cell diameter. This was expected and related to the increasing number of nucleating sites available at higher CFA concentration. Finally, Figures 2(c,d) show that increasing mold temperature (fixed NCC content of 3% and CFA of 1%) decreased the skin thickness which is related to lower heat transfer rate (small temperature difference) between the polymer melt and the mold walls. Overall, structural foams with a foamed core surrounded by two unfoamed skins were produced,[21,39] and a closed-cell structure was obtained.

**Layer Thickness.** Both core and skin thicknesses were measured based on SEM images (25×) and reported in Figure 3. In each image, the relative top skin, core and bottom skin thicknesses are presented relative to the total sample thickness. As expected, increasing the mold temperature from 30°C to 80°C decreased the skin thickness (increased core thickness), especially at low CFA content (the upper part of Figure 3). As mold temperature increased, the lower temperature difference between the polymer melt and the mold wall led to low heat transfer rates and the core layer had more time to develop its foamed structure.[40] But the core thickness also depends on NCC and CFA concentrations. Increasing NCC content from 0 to 5wt % increased the core thickness in all cases showing the nucleating role of NCC. For example, increasing NCC content from 0% to 5% increased by 45% and 30% the core thickness (1% CFA) at 30°C and 80°C mold temperature, respectively, which was more significant than 15% and 11% increase for samples containing 2% CFA. Figure 3 also shows that CFA content has a strong effect on layer thicknesses, especially at low NCC content (up to 3%). Increasing CFA from 1% to 2% increased the core thickness by about 22% and 20% at 0.5wt % NCC with 30°C and 80°C mold temperature, respectively. Thicker cores with increasing CFA concentration is because of more gas available in the polymer melt improving cell nucleation and cell growth dynamics vs part solidification.

**Cell Size and Density.** Cell density as a function of cell size is presented in Figure 4. The results show that increasing NCC content decreased the average cell diameter and increased cell density for all cases. For example, increasing NCC content from 0 to 5wt % at a mold temperature of 30°C and a CFA content of 1% decreased the cell diameters by around 42%, while increased the cell density by a factor of 5. These results confirm that NCC acts as a nucleating agent. The effect of CFA content is also shown in Figure 4. As expected, increasing the CFA content from 1% to 2% increased the number of nucleating sites, at both mold temperature, and increased cell density while

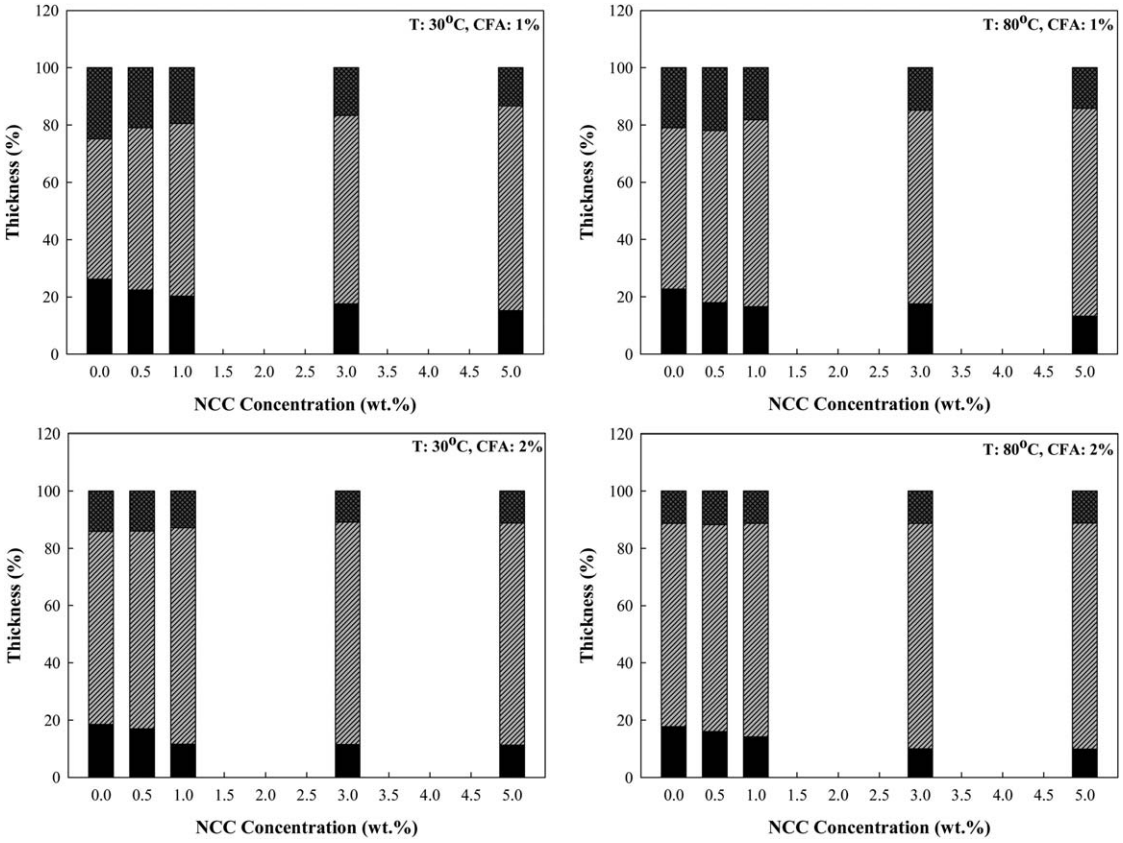


**Figure 3.** Relative skin (filled) and core (dashed) thicknesses for the nano-composite foams.

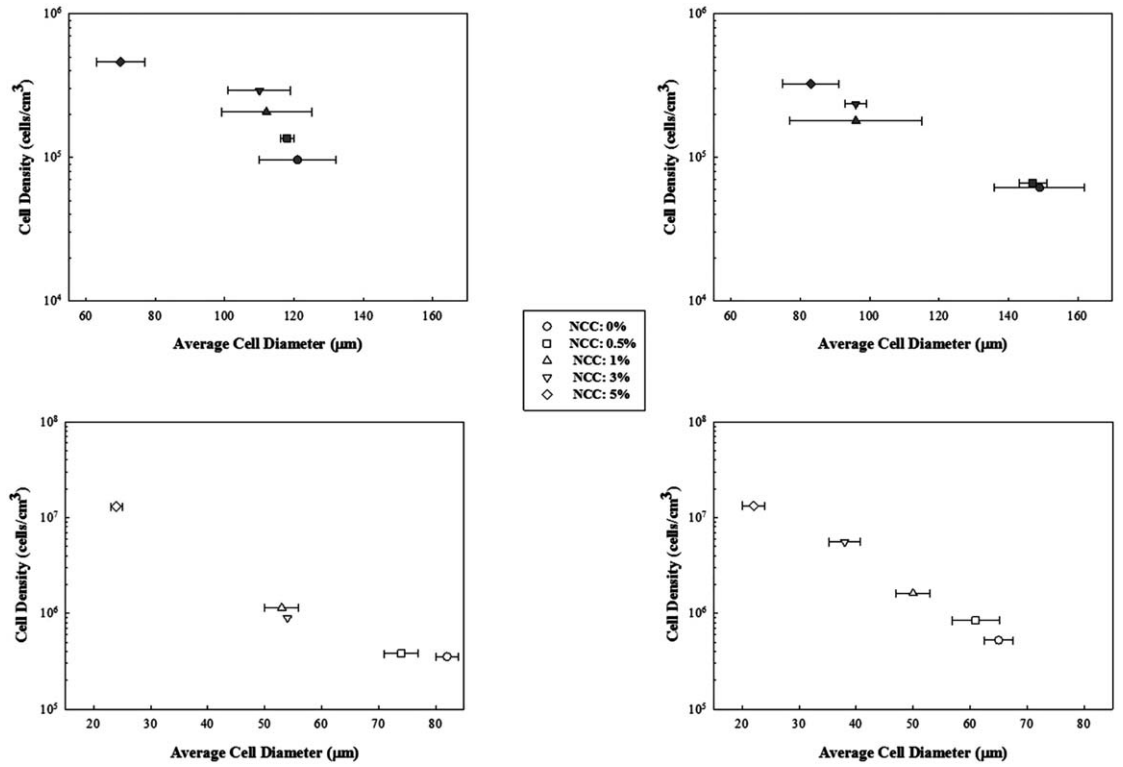


**Figure 4.** Cell density as a function of average cell diameter for the nano-composite foams at different mold temperature: 30°C (left column) and 80°C (right column). Closed symbols: 1% CFA and open symbols: 2% CFA.

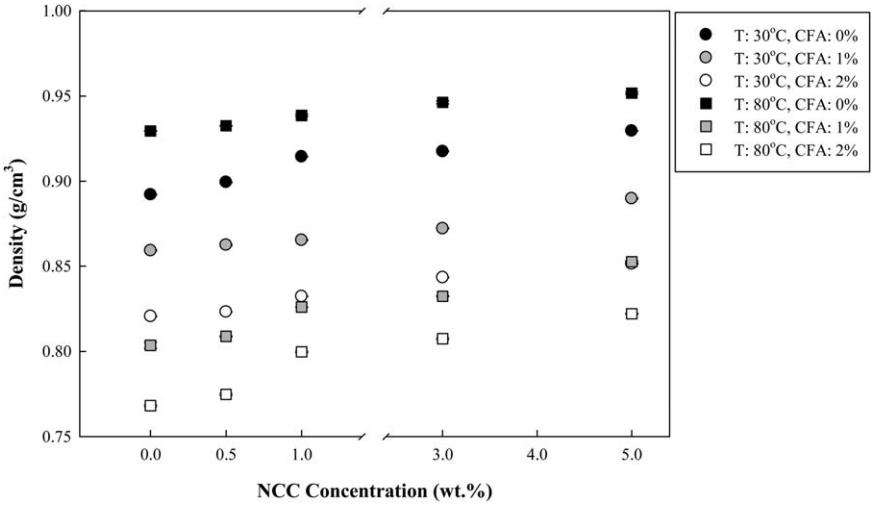


**Figure 5.** Density as a function of NCC content.

decreasing cell size: 37% cell size reduction and 2.8 times cell density increase for samples with 0.5wt % NCC at a mold temperature of 30°C. Similar results have been reported for agave fiber-high density polyethylene and wood fiber–polypropylene systems.[20,41] Finally, mold temperature also affects the thickness of each layer as mentioned before.[42] Increasing mold temperature led to thicker core, providing there is enough space for potential nucleating sites to be developed and improve the foam structure with well distributed smaller cells. For instance, increasing mold temperature from 30°C to 80°C led to changes in cell size and cell density from 54 μm and $0.90 \times 10^6$ cells/$cm^3$ to 38 μm and $5.57 \times 10^6$ cells/$cm^3$ respectively, for samples with 3wt % NCC and 2% CFA (−30% in cell diameter and +6.2 times in cell density).

## Physical Property

**Density.** Density results are presented in Figure 5 which can be compared with the density of neat PP (0.90 g/$cm^3$) and NCC (1.56 g/$cm^3$). Since NCC density is higher than PP, this explains why sample density increases with increasing NCC content. But this increase was less than 4% for all samples molded at 30°C, while the values are between 2% and 7% at 80°C for the composites and foams, respectively. As expected, increasing CFA content decreased density because of more gas available to foam the polymer melt.

The mold temperature had a minor effect on final foams density mostly because density is controlled by the amount of material injected (shot size). Nevertheless, as mold temperature increased from 30°C to 80°C, an average density decrease of 5% was observed with increasing NCC content from 0 to 5wt % and CFA content from 1% to 2%.

## Mechanical Properties

**Tension.** Tensile properties are presented in Figures 6–8. Figure 6 shows the effect of NCC and CFA content, as well as mold temperature on the specific Young's modulus ($E_S$). Increasing NCC concentration from 0 to 5wt % improved $E_S$ of both composite (18–22%) and foam (15–22%) samples. This clearly shows that NCC is a reinforcement agent because of its intrinsic high modulus (6.5 GPa) compared to PP (0.60 GPa).[36] Even if PP is a nonpolar thermoplastic, the tensile modulus improvements reported

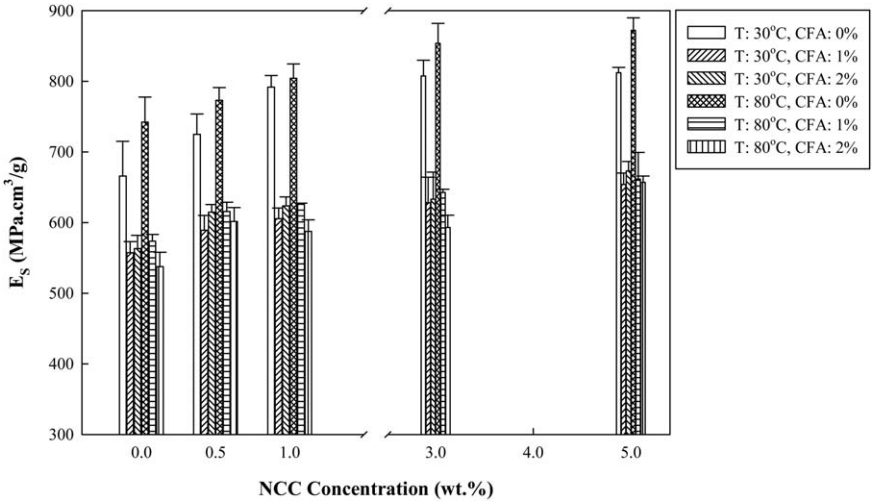


**Figure 6.** Specific tensile modulus as a function of NCC content.

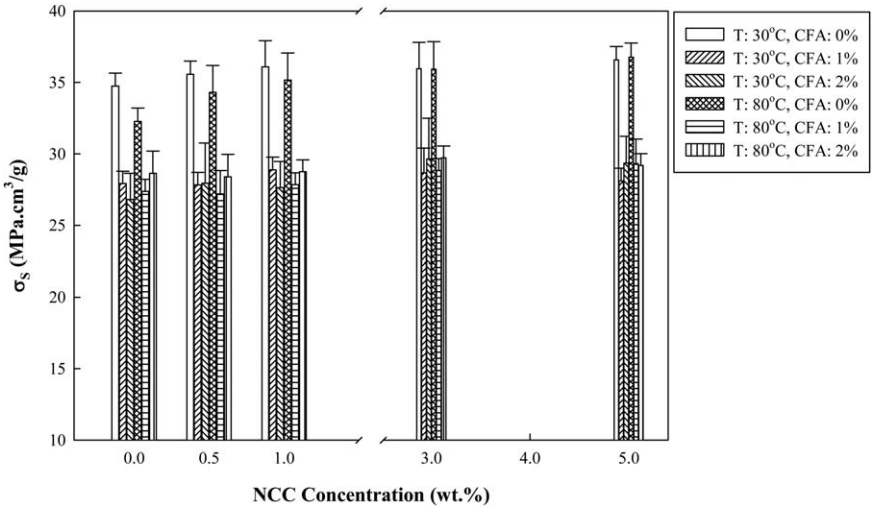


**Figure 7.** Specific tensile strength as a function of NCC content.

here with NCC, which is a polar material, are comparable with NCC-PA6 composites as reported elsewhere.[32] It is also worth mentioning that this low amount of NCC was able to better improve tensile modulus than micron-size particles at higher content. For example, increasing hemp (500 μm) content from 0% to 10–20% was shown to improve the tensile modulus of PP by only 13%.[43]

CFA content also has a direct effect on $E_S$, as less material is available to sustain the applied stresses,[44] $E_S$ decreased when compared to the solid matrix (unfoamed PP), especially when increasing CFA from 0% to 1% (from 872 to 662 MPa.cm$^3$/g for samples at 5wt % NCC and 80°C mold temperature). However, increasing CFA content from 1% to 2% did not significantly reduced the tensile modulus of samples molded at 30°C (less than 3.5%), but decreased their density by around 5%, so these $E_S$ values showed a marginal increasing trend compared to 1% CFA samples (average of 2.5% for NCC content of 0 to 5wt %). Finally, the effect of mold temperature on tensile modulus was found to be negative because of skin thickness reduction:[45] increasing TM from 30°C to 80°C mostly affects the $E_S$ of samples at 2% CFA compared to unfoamed samples (−10%). However, because of slightly lower density at higher mold temperature, $E_S$ values at 80°C are slightly higher than samples molded at 30°C.

Figure 7 presents the specific tensile strength ($\sigma_S$) of the samples. In this case the overall trend is similar to $E_S$. NCC content (0 to 5%) mostly affects $\sigma_S$ of composite samples (5–14%), for foam samples this increase was less than 10%. Plotting tensile strength as a function of fiber concentrations usually indicates the quality of the fiber–matrix interfacial bonding (adhesion). It can be concluded that relatively good adhesion between NCC and PP was achieved here.[20] $\sigma_S$ values were influenced by CFA content, especially when it increased from 0% to 1% (−20%). Mold temperature also had a small effect on specific tensile strength of all the samples.

The results for specific elongation at break ($\varepsilon_S$) are reported in Figure 8. As expected, addition of rigid particles like NCC decrease substantially the values for $\varepsilon_S$.[20] This reduction was observed for all the samples, but more noticeable in composites

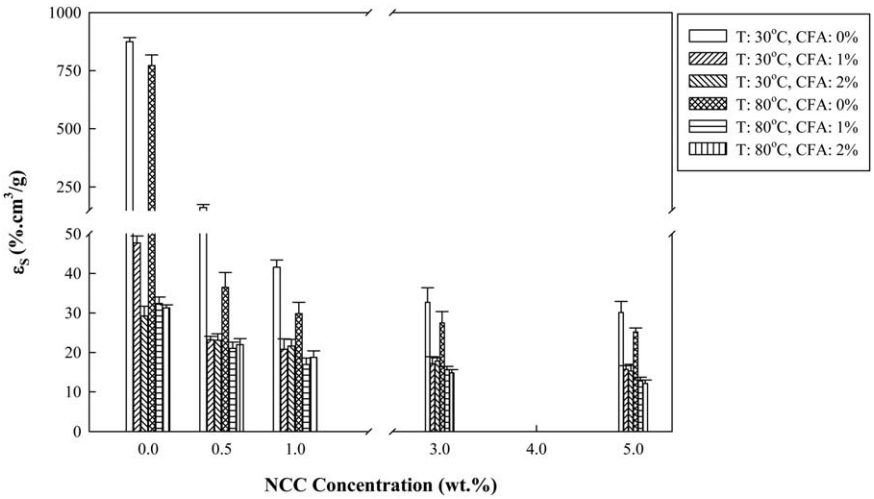


**Figure 8.** Specific elongation at break as a function of NCC content.

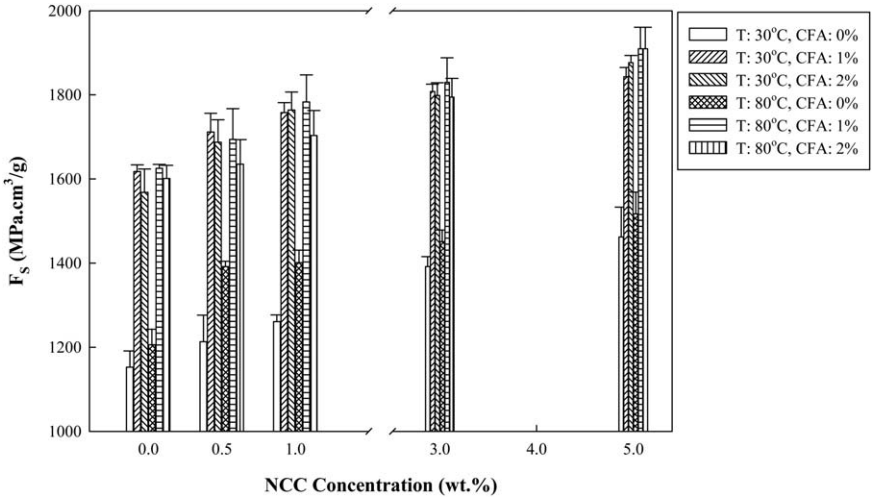


**Figure 9.** Specific flexural modulus as a function of NCC content.

when NCC increased from 0 to 0.5wt % (from 874 to 161%.cm$^3$/g at 30°C mold temperature). CFA increase also decreased $\varepsilon_S$, especially when increasing from 0% to 1%: a decrease from 161 to 23%.cm$^3$/g in samples containing 0.5wt % NCC at 30°C. Mold temperature had a slight effect on $\varepsilon_S$. For example, samples containing 5wt % NCC and 1% CFA produced a $\varepsilon_S$ decreased from 16 to 13%.cm$^3$/g when the mold temperature increased from 30°C to 80°C.

**Flexion.** Specific flexural modulus ($F_S$) results are presented in Figure 9. It can be seen that $F_S$ increased with increasing NCC. For the composites, a substantial increase (21%) between 0 and 3wt % NCC was observed which still increased at 5% NCC (27%) compared to neat PP. For the foam samples, $F_S$ increased by about 15–20% for NCC content of 0 to 5wt % for both mold temperatures which could be related to relatively good interfacial bonding between NCC and PP allowing good stress transfer from the matrix to the nano-particles.[20,29] As expected, this increase was lower than reported in our previous work because a polar matrix (PA6) was used.[32] Nevertheless, the results show the potential of NCC to increase flexural property of both PP composites and foams at low filler content. It is worth mentioning that all foam samples have higher $F_S$ than their unfoamed counterparts. As reported in previous works,[34,35] higher specific mechanical property can be obtained for foams compared to unfoamed samples. Increasing CFA content up to 2% increased even more the $F_S$ values of all samples (24–36%). Finally, the effect of mold temperature, as can be seen in Figure 9, is marginal. At higher mold temperature (lower skin thickness), lower mechanical properties are expected[45] and this is the case here but most of the samples show the inverse trend because of different density profile as discussed in previous section.

**Impact.** The results of specific impact strength ($I_S$) are presented in Figure 10. All composite and foam samples showed a decreasing $I_S$ trend with increasing NCC content. As NCC increased from 0 to 5wt %, $I_S$ decreased by around 15–19% for composites and 12–13% for foam samples. These results were expected as the presence of rigid nano-particles increase the interfacial area between the matrix and the fibers and helps probable crack initiation and

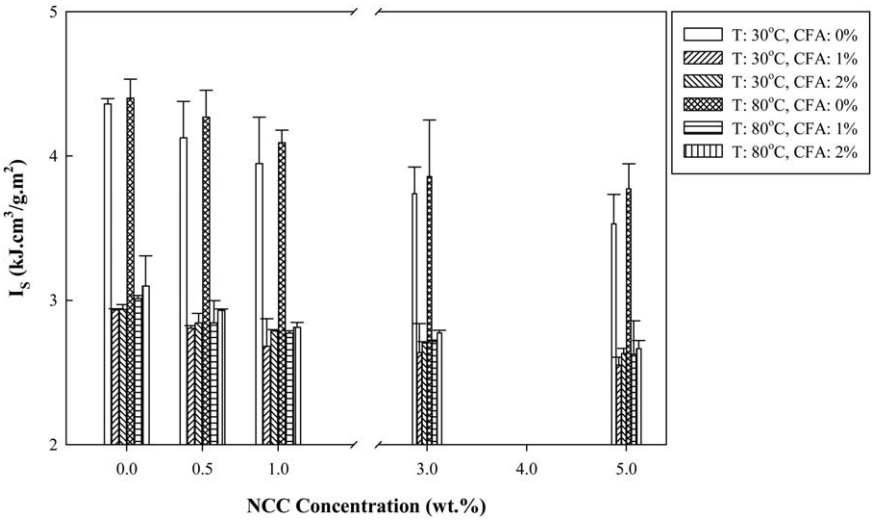


**Figure 10.** Specific impact strength as a function of NCC content.

propagation.[32,33] CFA addition, especially at 1%, decreased the $I_S$ by about 30% compared to their composite counterparts at both mold temperatures. Like other properties, $I_S$ value at 2% CFA is higher than samples with 1% CFA which can be related to lower density. For example, the sample containing 0.5wt % NCC at a mold temperature of 80°C has $I_S$ values of 2.93 and 2.84 kJ.cm$^3$/g.m$^2$ for 2% and 1% CFA, respectively. Finally, as observed for the other properties studied, increasing mold temperature from 30°C to 80°C decreased $I_S$ mostly because of thinner skins.

## CONCLUSION

Nano-composite foams based on NCC and PP were prepared via extrusion coupled with injection molding. The effect of three parameters was studied: NCC concentration (0–5wt %), foaming agent content (0–2wt %), and mold temperature (30°C and 80°C). From the samples produced, complete morphological (layer thickness, cell size, and cell density), physical (density), and mechanical (tension, flexion, and impact) characterization of the samples was performed. From the results obtained, several conclusions can be drawn.

Firstly, it was shown that it is possible to melt compound NCC in a hydrophobic matrix (PP). Secondly, NCC was shown to be an efficient nucleating agent as it was able to reduce cell size (42–71%) and increase cell density (5–37 times). Thirdly, NCC was shown to have high reinforcing potential. As its concentration increased from 0 to 5wt %, increased specific tensile modulus (15–22%), specific tensile strength (1–14%), and specific flexural modulus (13–26%) were obtained. Nevertheless, the materials were more brittle with lower specific impact strength (10–20%) and specific elongation at break (50–96%).

Finally, increasing foaming agent content decreased cell size and increased cell density because of increasing nucleating sites and more gas molecules available. Mold temperature mostly affected the core and skin thicknesses by imposing different heat transfer rates on the polymer melt. Increasing mold temperature also decreased skin thickness because there was more time available for cell nucleation and growth before the part solidified. All these morphological changes have a direct effect on the final mechanical properties of the structural foams produced.

## ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), as well as Arboranano. The technical support of Mr. Yann Giroux is also appreciated.

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