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Enhanced cellulose nanofibril/polypropylene composites for 3D printing

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Novel composites containing natural spray-dried nanofibers have improved rheological properties over conventional filled polypropylene composites and may be suitable for fused filament fabrication.

Polypropylene (PP) is one of the most widely used thermoplastics, but it is not typically used in 3D printing techniques (e.g., material extrusion) because it tends to shrink and warp during the printing process.[1,2] In previous work, however, it has been demonstrated that cellulose nanofibrils (CNFs)—because of their low thermal expansion coefficient—may be used to improve the processability of PP for 3D printing and to enhance the mechanical properties of PP printed parts.[3] The majority of the previous work in this field has focused on solution or solvent mixing processes for the manufacture of the composites. Indeed, it has been shown that when the nanofibers are well dispersed and distributed in the PP, the viscosity of the PP (at low shear rates) is generally increased.[4] Melt compounding of fibers (rather than solution or solvent mixing) with thermoplastics, however, is the most common industrial method used to make thermoplastic composites and so this process also warrants investigation.

To facilitate polymer processing during composite fabrication—and to successfully incorporate the nanofibers into the polymer melt—it is necessary for the fibers to be in a dry form.[5] Spray drying is a typical method for obtaining dry cellulose nanofibers from suspensions for such purposes, but the rheological properties of spray-dried-CNF-reinforced PP composites produced via injection molding—or fused filament fabrication (FFF)—have not yet been studied. Instead, the majority of earlier research has focused on the rheological behavior of PP reinforced with (more expensive) cellulose nanocrystals.[4,6]

In this study, we have therefore explored the rheological behavior of spray-dried-CNF-reinforced PP composites and have tested their processability for the FFF 3D printing method.[7] For our experiments we used a bench-scale material extrusion device with an estimated shear rate at the printing nozzle of 100–200s^{-1}.[8] This shear rate is much lower than that used in injection molding and meant that a parallel-plate rheometer was sufficient to obtain useful rheology information for our study.

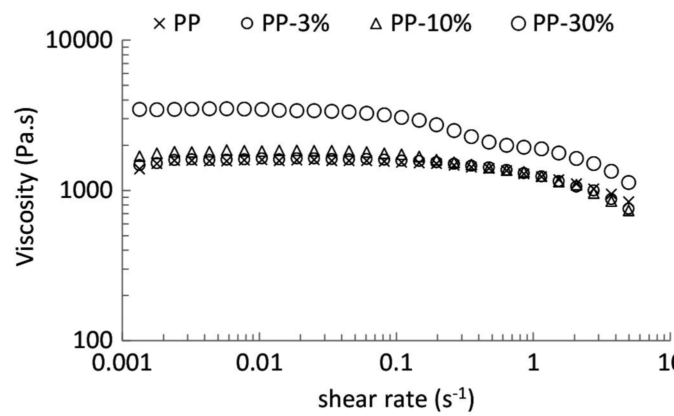

Figure 1. *Experimentally measured viscosity, as a function of shear rate, of neat polypropylene (PP) and PP composites filled with spray-dried cellulose nanofibrils (CNFs) at loadings of 3, 10, and 30wt%.*

To obtain the CNFs for our composites (listed in Table 1) we used a pilot-scale spray dryer to dry and dilute a suspension containing 1.2wt% CNFs. We then oven dried both the CNFs and maleic anhydride PP pellets (for two hours at 105°C) to remove any moisture before compounding. To produce our nanofiber-filled PP composites, we used a 'fast' rather than a conventional masterbatch production method. In our approach we used an increased screw speed of 250 revolutions per minute to reduce the residence time of CNF in the extruder and to increase the production volume.[7] In the next step of our fabrication process, we diluted the masterbatch pellets with fresh PP before extruding and pelletizing the mixture again and then injection molding the final plate-like samples.

We used a stress-controlled Bohlin Gemini rheometer (Malvern Instruments, UK) to study the rheological behavior of our composite samples. We conducted the tests, in air, at a temperature of 200°C, and used

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***Table 1.** Formulations of the PP and CNF/PP composite samples.*

Sample	PP (wt%)	CNF (wt%)
PP	100	0
PP-3%	97	3
PP-10%	90	10
PP-30%	70	30

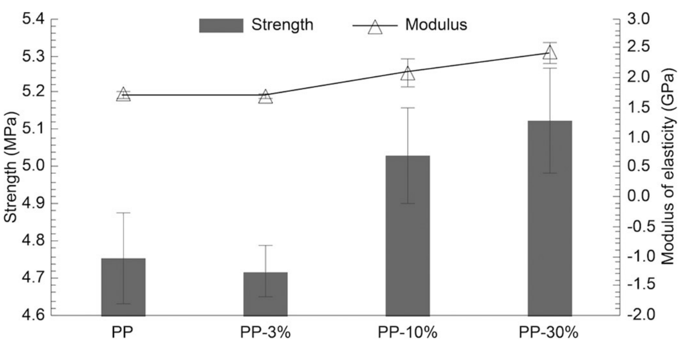

***Figure 2.** Measured flexural properties (strength and modulus of elasticity) of the PP and CNF/PP composites.*

parallel plates with a diameter of 25mm and a fixed gap size of 1mm. We cut the sheet-shaped test samples from our injection molded flexural bars and placed these between the plates. To investigate the nonlinear behavior of the samples, we conducted a steady shear flow test over a shear rate range of 0.001 to $5s^{-1}$. Our results (see Figure 1) show that the viscosity of PP filled with 30wt% CNF is higher than any of our other samples and that CNF loadings of 3 or 10wt% did not produce a significant change in the viscosity of PP. Furthermore, we find that the neat PP and composite samples all exhibited shear thinning behavior as the shear rate increased. Indeed, the viscosity of the composites decreased to close to that of pure PP once the shear rate was greater than $5s^{-1}$. The low viscosity we measured for the spray-dried-CNF-filled PP composites at high shear rates thus makes our materials suitable for FFF processing.

To test the effectiveness of our fast masterbatch production method for distributing CNFs within PP, we also conducted a series of mechanical tests (following the ASTM International D 790-10 standard) on our injection-molded flexural bars. As illustrated in Figure 2, we observe that the flexural properties of PP are improved when the CNF content of the composites is greater than 10wt%. For example, the flexural strength of the composites containing 10 and 30wt% CNF are 6 and 8% stronger than pure PP, respectively. We also find that the addition of large amounts of CNF into the PP reduces the stress concentration at the fiber ends. This improves the interfacial contact between the fibers and the matrix, and in turn induces crazing (i.e., the formation of a network of fine cracks) during the mechanical testing and contributes to the improved PP strength.[7] We thus confirmed that our fast materbatch production method is an effective way to distribute CNFs within a PP matrix. In addition, the flexural stiffness (modulus of elasticity) of our 10 and 30wt% composites is 22 and 42% greater, respectively, than the pure PP sample. We attribute this enhancement in stiffness to the intrinsic rigidity of CNFs.

In summary, we have investigated the use of spray-dried CNFs as reinforcements for PP composites in 3D printing. In particular, we studied the rheological and flexural properties of our composite samples. Our results show that the addition of up to 30wt% spray-dried CNFs into the PP matrix did not significantly alter the shear thinning behavior of the PP over the typical shear rate range used in FFF. We also found that our injection-molded CNF/PP composites exhibit improved mechanical properties compared with pure PP. In the next step of our work we will use these CNF/PP composites in FFF and test the properties of the fabricated samples.

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