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Melt- Processing of Polymer Nanocomposites with Cellulose Nanocrystals

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On account of their intriguing mechanical properties and potentially low toxicity, rod-like cellulose nanocrystals (CNCs) are increasingly used to reinforce polymers, and to produce nanocomposites with low density, and improved and controlled mechanical properties. While on a laboratory scale many intriguing nanocomposites made with CNCs have been made and were demonstrated to exhibit a significant improvement in mechanical properties over the neat polymers. Addressing this challenge, this dissertation deals with the investigation of approaches that permit the processing of polymer/CNC nanocomposites with industrially feasible melt-processing methods. Several cellulose types, various polymer systems, and different processing schemes were explored.

In a first foray, commercially available microcrystalline cellulose (MCC) was milled (gMCC) and compounded with poly(vinyl acetate) that had also been milled (gPVAc). The milled starting materials were pre-mixed and subsequently melt-mixed. As a benchmark, directly melt-mixed nanocomposites of cellulose nanocrystals isolated by acid hydrolysis from cotton and PVAc (PVAc/CNC) were prepared. Interestingly, the extent of reinforcement was the similar in the PVAc/CNC and gPVAc/gMCC composites.

Further, the fabrication of nanocomposites of polyamide 12 (PA12) and CNCs isolated from cotton and tunicates was explored. Through a comparative study that involved solution-cast and melt-processed materials, it was shown that PA12/CNC nanocomposites with ultimate mechanical properties can be prepared in a process that appears to be readily scalable to an industrial level. The results demonstrate that CNCs isolated from the biomass by phosphoric acid hydrolysis display both a sufficiently high thermal stability to permit melt-processing with PA12. Thus, PA12/CNC nanocomposites prepared by melt-mixing the two components in a co-rotating roller blade mixer and subsequent compression molding display mechanical properties that are comparable to those of solution-cast reference materials. Young's modulus and maximum stress could be doubled in comparison to the neat PA12 by introduction of 10% (CNCs from tunicates) or 15% w/w (CNCs from cotton) CNCs.

Finally, it is shown that a commercially accessible nanocrystal source, a particular grade of MCC, can easily be converted into thermally stable CNCs by ultrasonication in phosphoric acid. A scalable melt-mixing process was used to produce nanocomposites of these CNCs with a thermoplastic polyurethane (TPU) elastomer. A significant improvement of the room temperature storage modulus from 40 MPa (neat polymer) to 120 MPa (10% w/w CNC) was observed. The introduction of CNCs not only increased the stiffness of the polymer matrix, but also improved the shape memory properties of the nanocomposite.

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