SPE SOCIETY OF PLASTICS ENGINEERS
Plastics Research Online
10.2417/spepro.006913

Developing greener composites from cellulose nanocrystals and biopolyurethane

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Environmentally friendly nanocomposite materials from bio-based polyurethane and cellulose nanocrystals show significantly improved mechanical properties with only 1% nanocrystal filler.

Over the past few decades, increasingly widespread interest in sustainable development has led research efforts in the production of materials from renewable resources to grow exponentially. In particular, considerable effort is currently devoted to replacing synthetic reinforcements in composites with natural fibers or particles, a result of the renewability and low environmental impact of these natural materials.[1] Following this trend, we have prepared nanocomposite materials from a waterborne polyurethane (WBPU) and cellulose nanocrystals (CNCs). The WBPU is formulated from a bio-based monomer—Agrol 3.6 from BioBased Technologies, a hydroxylated soybean oil—in water, avoiding the use of polluting solvents. In addition, the CNC filler is sourced from inexpensive forestry industry materials, and adds significant value to the composites. Here, we present our synthetic methodology, and the mechanical, physical, and thermal properties of the resulting WBPU/CNC nanocomposite films.[2]

We obtain the CNCs by acid hydrolysis of a commercial microcrystalline cellulose material. Solvent exchange of the aqueous CNC suspension with acetone is performed and the resulting CNC dispersion is mixed with the dried macrodiol using a homogenizer. After solvent evaporation, we prepare the nanocomposites by adding a 4,4′-diphenylmethane diisocyanate pre-polymer and dibutyltin dilaurate catalyst, and pour the resulting mixture into a pre-heated mold (80°C). The mold is closed and pressed at 0.5MPa and 80°C for 2h then transferred to an oven at the same temperature for 16h.

Using this method, we prepared neat WBPU and composites with CNC concentrations of 0.5, 1, and 2% by weight (wt%). The nanocomposite films are yellow in color and transparent even at 2wt% CNC. Furthermore, we assessed the CNC dispersion in the nanocomposites under crossed polarized light and found that the CNCs are uniformly distributed in the WBPU matrix (see Figure 1).

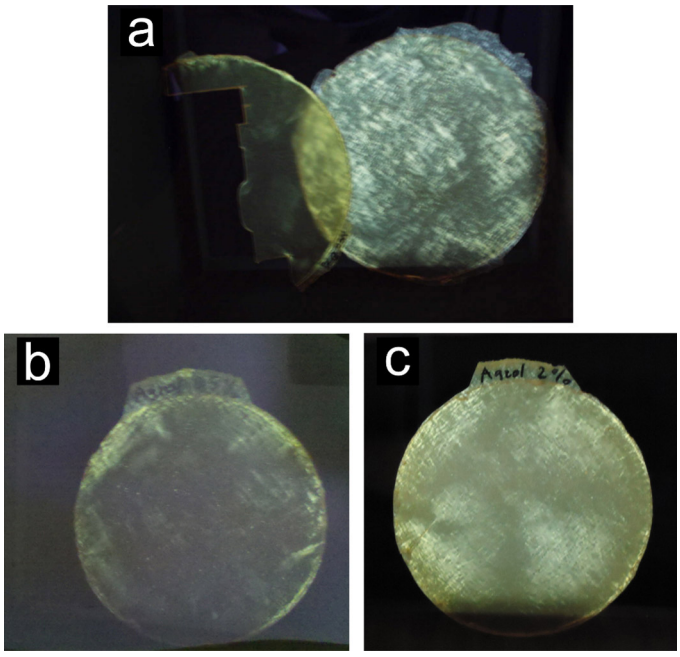

Figure 1. *Photographic images of waterborne polyurethane/cellulose nanocrystal (WBPU/CNC) composite materials obtained under crossed polarized light: neat WBPU (a, left) and composites containing 0.5% by weight (wt%) (b), 1wt% (a, right), and 2wt% (c) CNC filler.*

Including CNCs in the matrix increases the glass transition temperature of the composites—the temperature at which a material changes from a hard 'glassy' state to a rubber-like state—from 31°C in neat WBPU to 35°C in the 2wt% CNC sample, a result of restriction in the movement of the polymer chains. In addition, the storage modulus (the elastic response of a material under dynamic shear) of

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the 2wt% nanocomposite in the rubbery plateau region is significantly higher than that of neat WBPU. We also evaluated the thermal degradation properties of the samples by thermogravimetric analysis, which showed similar characteristics regardless of the amount of CNC present in both air and nitrogen atmospheres. This indicates that the CNC filler is well coated in the matrix and hence no additional degradation occurs.

It is well known that when the CNC concentration reaches the percolation threshold—the point at which infinite connectivity of the filler occurs—the mechanical properties of the composite greatly increase. However, above an optimum point, further CNC addition leads to agglomeration and an associated reduction in the mechanical properties,[3,4] a trend observed in this study. For example, the elastic modulus (a measure of the stiffness of a material) of the 1wt% CNC sample is over four times that of neat WBPU and the tensile strength is more than doubled (see Figure 2). Above percolation, however, the 2wt% CNC composite shows significant decreases in both elastic modulus and tensile strength to below the values obtained for neat WBPU.

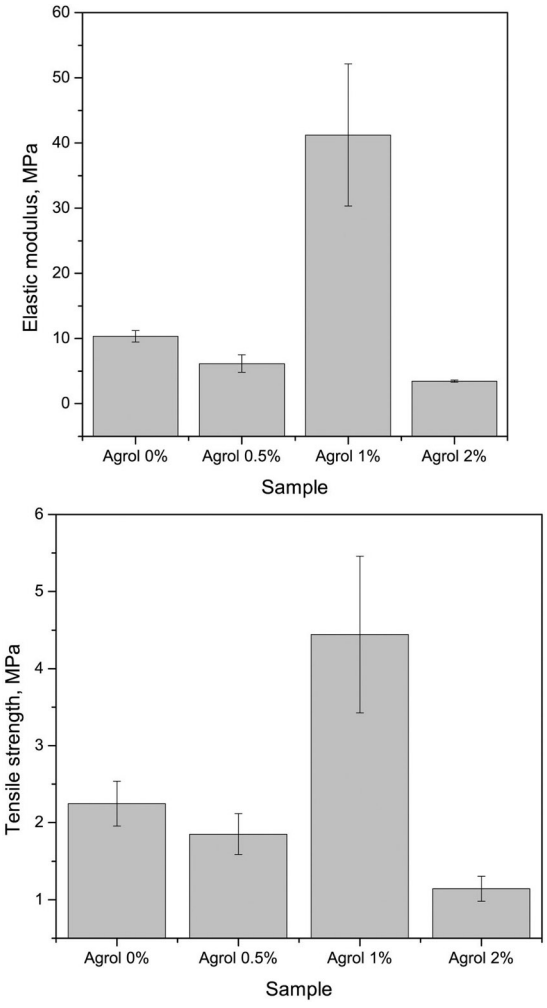

Figure 2. *The elastic modulus (top) and tensile strength (bottom) of WBPU/CNC nanocomposites containing 0–2wt% filler. Agrol: Bio-based WBPU source.*

In summary, we have significantly improved the mechanical properties of a bio-based WBPU using CNCs, a nanofiller that is also a natural polymer. Notably, the amount of filler required to achieve this improvement is remarkably low, and higher CNC concentrations have a negative effect. These results show the properties of bio-based PUs are easily tailored by CNC addition. Our future work in this area will include focusing on greener WBPUs, increasing the bio-generated raw material content of the WBPUs, and further investigating CNC addition to develop materials with competitive properties.

The authors acknowledge the financial support provided by the National Scientific and Technical Research Council (CONICET): Multi-year Research Project 0866, the National Agency for the Promotion of Science and Technology (ANPCyT): Scientific and Technological Research Project 0732, the National University of Mar del Plata (UNMdP), and the Bio-based Polyurethane Composites with Natural Fillers (BIOPURFIL) Project (PIRSES-GA-2012-318996).

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References

1. S. H. Park, K. W. Oh, and S. H. Kim, *Reinforcement effect of cellulose nanowhisker on bio-based polyurethane*, **Compos. Sci. Technol. 86**, pp. 82–88, 2013. doi:10.1016/j.compscitech.2013.07.006
2. V. L. Mucci, A. Ivdre, J. M. Buffa, U. Cabulis, P. M. Stefani, and M. I. Aranguren, *Composites made from a soybean oil biopolyurethane and cellulose nanocrystals*, **Polym. Eng. Sci.**, 2017. doi:10.1002/pen.24539
3. X. Cao, H. Dong, and C. M. Li, *New nanocomposite materials reinforced with flax cellulose nanocrystals in waterborne polyurethane*, **Biomacromolecules 8**, pp. 889–904, 2007. doi:10.1021/bm0610368
4. M. I. Aranguren, N. E. Marcovich, and M. A. Mosiewicki, *17: Mechanical performance of polyurethane (PU)-based biocomposites*, **Biocomposites: Design and Mechanical Performance (Woodhead Publishing, 1st edn)**, pp. 465–486, 2015.