

Nanocellulose reinforced polyurethane hydrogels

J. Sierke¹, D. Heath¹, B. McGraw², A.V. Ellis^{1*}

¹School of Chemical and Biomedical Engineering, University of Melbourne, Parkville, Victoria, 3010, Australia

²Ohio Soybean Council, 918 Proprietors Rd, Worthington, Ohio, 43082, United States of America

Keywords: nanocellulose, polyurethane, hydrogels, biomedical materials.

Presenting author email: amanda.ellis@unimelb.edu.au

Nanocellulose consists of nano-sized particles, ranging in size from 5-70 nm in diameter, including cellulose nanocrystals (CNC) and cellulose nanofibers (CNF), which range in average length from 100-250 nm or up to several micrometres, respectively (Mishra et al., 2018). Nanocellulose is a renewable resource that can be isolated from a wide range of cellulosic materials, including agricultural waste materials such as wheat, barley and rice straws (Oun and Rhim, 2016), pistachio nut shells (Kasiri and Fathi, 2018), and banana peel (Khawas and Deka, 2016). Nanocellulose is also biodegradable (Singh et al., 2016), and has been shown to possess negligible cytotoxicity (Endes et al., 2016).

As such there is great interest in incorporating nanocellulose into polymeric materials as a reinforcing agent, particularly for biomedical applications. In this work, nanocellulose has been isolated from bleached pea straw mulch using a combination of chaotropic agents (e.g., zinc chloride (ZnCl₂) or urea) and blending. Analysis of the nanocellulose by high resolution transmission electron microscopy (HRTEM) (Figure 1) shows that blending bleached pea straw mulch for 30 min or 60 min in MilliQ water (no chaotropic agents) yielded a mixture of nanofibers and microfibrils of cellulose. In comparison, blending bleached pea straw mulch in aqueous solutions of ZnCl₂ or ZnCl₂/urea yielded flat plates of cellulose, with the maximum width of the plates varying from approximately 420 nm to 1060 nm.

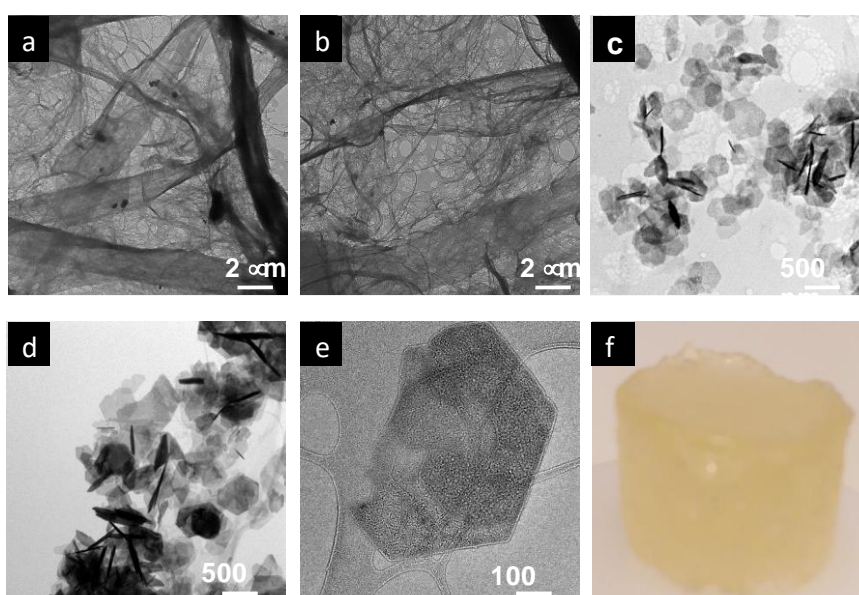


Figure 1. TEM images of the solids isolated from 0.2 wt% solutions of twice treated pea straw after (a) 30 min blending in MilliQ water, (b) 60 min blending in MilliQ water, (c) 30 min blending in ZnCl₂/urea/MilliQ water, and (d) 30 min blending in ZnCl₂/MilliQ water, (e) 30 min blending in ZnCl₂/MilliQ water and (f) example 0.1 wt% nanocellulose cross-linked polyurethane hydrogel.

The isolated nanocellulose was then incorporated into polyurethane hydrogels at various loading (0-1 wt%) using a combination of polyethylene glycol (PEG, $M_n \sim 1000$) and 1,6-hexamethylene diisocyanate (HDI).

In order to maintain a good dispersion of nanocellulose, the nanocellulose was first mixed with PEG in solutions of ethanol and then dried under vacuum. The dried PEG/nanocellulose mixture was reacted with HDI in *N*-methylpyrrolidone to yield the polyurethane. The resulting polyurethanes were analysed by attenuated total reflectance - infrared Fourier transform spectroscopy, scanning electron microscopy, thermal gravimetric analysis, X-ray diffraction and compression mechanical tests. Mechanical testing of polyurethane hydrogels swollen with phosphate-buffered saline (PBS) was also performed as well as cytotoxicity tests. The results obtained showed

that incorporating nanocellulose into polyurethane hydrogels improves the mechanical integrity of the polyurethane even in the swollen state, while showing a good dispersion of nanocellulose throughout the hydrogel with limited cytotoxicity.

We would like to thank the Ohio Soybean Council, USA for providing the funding for this work, and the Melbourne Advanced Microscopy Facility at the University of Melbourne for providing access to the HRTEM.

Endes, C., Camarero-Espinosa, S., Mueller, S., Foster, E. J., Petri-Fink, A., Rothen-Rutishauser, B., Weder, C. & Clift, M. J. D. 2016. A critical review of the current knowledge regarding the biological impact of nanocellulose. *Journal of Nanobiotechnology*, 14, 78.

Kasiri, N. & Fathi, M. 2018. Production of cellulose nanocrystals from pistachio shells and their application for stabilizing Pickering emulsions. *International Journal of Biological Macromolecules*, 106, 1023-1031.

Khawas, P. & Deka, S. C. 2016. Isolation and characterization of cellulose nanofibers from culinary banana peel using high-intensity ultrasonication combined with chemical treatment. *Carbohydrate Polymers*, 137, 608-616.

Mishra, R. K., Sabu, A. & Tiwari, S. K. 2018. Materials chemistry and the futuristic eco-friendly applications of nanocellulose: Status and prospect. *Journal of Saudi Chemical Society*.

Oun, A. A. & Rhim, J.-W. 2016. Isolation of cellulose nanocrystals from grain straws and their use for the preparation of carboxymethyl cellulose-based nanocomposite films. *Carbohydrate Polymers*, 150, 187-200.

Singh, G., Chandoha-Lee, C., Zhang, W., Renneckar, S., Vikesland, P. J. & Pruden, A. 2016. Biodegradation of nanocrystalline cellulose by two environmentally-relevant consortia. *Water Research*, 104, 137-146.