

PHOTO-CURABLE THIOL-ENE / NANOCELLULOSE ELASTOMERIC COMPOSITES FOR BIO-INSPIRED AND FLUORINE-FREE SUPERHYDROPHOBIC SURFACES

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Cellulose nanofibrils are attractive candidate biomaterials for polymer composites owing to their superior characteristics compared to organic resins such as biocompatibility, biodegradability, process-induced anisotropy of the composite due to high aspect ratio, tunable surface chemistry and reinforcement capability; however, the widespread utilization of these biobased materials remains limited, especially for applications involving photopolymerization [1]. In this work, a photo-curable thiol-ene resin containing controlled concentrations of cellulose nanofibrils oxidized by 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) mediation (TOCNF) is prepared without dispersants or surfactants owing to surface modifications such as counter cation exchange of carboxyl and grafting of thiol and ene functional moieties. The rheological and photo-crosslinking behavior of the TOCNF suspensions, the thermal stability and the mechanical performance of the cured composite materials, and the hydrophobicity of lotus-replicated hierarchical surfaces are characterized [2]. The composite suspensions are shear thinning with power law exponents around 0.3 and their photo-conversion profiles significantly vary based on the grafted surface functionality with thiol modifiers causing a lower curing rate than enes. The cured composites show improved thermal resistance at elevated degradation temperatures above $\sim 360^{\circ}\text{C}$, and outperform the neat thiol-ene polymer in terms of hardness (x5.8) and reduced modulus (x3.4). Moreover, the surface of composites texturized with a lotus leaf pattern is superhydrophobic with a water contact angle of 155° , higher than that of the neat and texturized polymer (147°). This was achieved without any surface treatment such as fluorination [3]. These results are useful to obtain mechanically and thermally robust photo-curable elastomers as well as to explore the potential of such composite resins in manufacturing processes requiring rapid curing such as 3D printing and roll-to-roll processing.

[1] Poothanari M.A., Schreier A., Missoum K., Bras J., Leterrier Y., *ACS Sustainable Chem. Eng.* 10, 3131 (2022).

[2] González Lazo M.A., Katrantzis I., Dalle Vacche S., Karasu F., Leterrier Y., *Materials*, 9, 738 (2016).

[3] Wasser L., Dalle Vacche S., Karasu F., Müller L., Castellino M., Vitale A., Bongiovanni R., Leterrier Y., *Coatings*, 8, 436 (2018).