Stable Polyurethane Containers through the Assembly of Cellulose Nanocrystals at the Oil Droplet Interface and Crosslinking with Polymeric Isocyanate

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Nanocelluloses exhibit unique properties resulting from their structure and surface chemistry. These give rise to their capability to assemble at oil–water interfaces and impart new functionality to emulsion and latex systems. In this study we report on the preparation of the polyurethane (PU) containers *via* polymerization at the oil/water interface of Pickering emulsion stabilized by nanocrystalline cellulose (NCC) with the following direct crosslinking of the shell by reaction between NCC hydroxyl groups and polymethylene polyphenylene isocyanate (PAPI) dissolved in the oil core. Unlike the previously reported PU containers containing NCC only as a reinforcing agent, in our study, NCC was employed simultaneously as an emulsion stabilizer and a source of hydroxyl groups to crosslink the shell with urethane linkages. In this direct crosslinking, NCC behaved like a branched oligo-polyol of high functionality (6 hydroxyl groups per monomer unit) with short chains derived from hydroxyl groups. As a consequence, the capsule shell appeared as a highly crosslinked polyurethane structure with increased rigidity due to the high density of hard domains formed by urethane groups.

Considering energy storage applications, the NCC/PU capsules were loaded with organic phase-change material (PCM) *n*-Octadecane by dissolving in the oil core. The resulted capsules were studied with Fourier-transform infrared spectroscopy (FTIR), fluorescent confocal microscopy, scanning and transmittance electron microscopy. FTIR spectroscopy confirmed the formation of polyurethane in reaction between NCC hydroxyl groups and PAPI isocyanate groups along with successful encapsulation of *n*-Octadecane. Confocal microscopy demonstrated that all PAPI stained with the Nile Red dye participated in the shell formation. The electron microscopy confirmed the formation of uniform and smooth capsule shell with an average thickness of 450±60 nm.

The latent heat storage properties, thermal reliability, shape and thermal stability of NCC/PU capsules were studied with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and infrared thermal imaging. The DSC demonstrated the latent heat storage capacity of the resulted capsules was 79 J g^{-1}. The cyclic DSC test did not reveal any changes in latent heat storage and release properties after 20 heating/cooling cycles. TGA and thermal imaging demonstrated that the encapsulation *n*-octadecane within NCC/PU capsules improved its thermal stability and effectively prevented leakage in the liquid state, which is the main issue with organic PCMs

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