Porous Materials from Cellulose Nanofibrils

NICHOLAS TCHANG CERVIN

Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Friday the 21st November 2014, at 10:00 a.m. in F3, Lindstedtsvägen 26, KTH, Stockholm.
Abstract

In the first part of this work a novel type of low-density, sponge-like material for the separation of mixtures of oil and water has been prepared by vapour deposition of hydrophobic tri-chloro-silanes on ultra-porous cellulose nanofibril (CNF) aerogels. To achieve this, a highly porous (>99%) robust CNF aerogel with high structural flexibility is first formed by freeze-drying an aqueous suspension of the CNFs. The density, pore size distribution and wetting properties of the aerogel can be tuned by selecting the concentration of the CNF suspension before freeze-drying. The hydrophobic light-weight aerogels are almost instantly filled with the oil phase when they selectively absorb oil from water, with a capacity to absorb up to 45 times their own weight. The oil can subsequently be drained from the aerogel and the aerogel can then be subjected to a second absorption cycle.

The second part is about aerogels with different pore structures and manufactured with freeze-drying and supercritical carbon dioxide for the preparation of super slippery surfaces. Tunable super slippery liquid-infused porous surfaces (SLIPS) were fabricated through fluorination of CNFs and subsequent infusion with perfluorinated liquid lubricants. CNF-based self-standing membranes repelled water and hexadecane with roll-off angles of only a few degrees. The lifetime of the slippery surface was controlled by the rate of evaporation of the lubricant, where the low roll-off angle could be regained with additional infusion. Moreover, adjusting the porosity of the membranes allowed the amount of infused lubricant to be tuned and thereby the lifetime. The CNF-based process permitted the expansion of the concept to coatings on glass, steel, paper and silicon. The lubricant-infused films and coatings are optically transparent and also feature self-cleaning and self-repairing abilities.

The third part describes how porous structures from CNFs can be prepared in a new way by using a Pickering foam technique to create CNF-stabilized foams. This technique is promising for up-scaling to enable these porous nanostructured cellulose materials to be produced on a large scale. With this technique, a novel, lightweight and strong porous cellulose material has been prepared by drying aqueous foams stabilized with surface-modified CNFs. Confocal microscopy and high-speed video imaging show that the long-term stability of the wet foams can be attributed to the octylamine-coated, rod-shaped CNF nanoparticles residing at the air-liquid interface which prevent the air bubbles from collapsing or coalescing. Careful removal of the water yields a porous cellulose-based material with a porosity of 98%, and measurements with an autoporosimeter (APVD) reveal that most pores have a radius in the range of 300 to 500 μm.

In the fourth part, the aim was to clarify the mechanisms behind the stabilizing action of CNFs in wet-stable cellulose foams. Factors that have been investigated are the importance of the surface energy of the stabilizing CNF
particles, their aspect ratio and charge density, and the concentration of CNF particles at the air-water interface. In order to investigate these parameters, the viscoelastic properties of the interface have been evaluated using the pendant drop method. The properties of the interface have also been compared by foam stability tests to clarify how the interface properties can be related to the foam stability over time. The most important results and conclusions are that CNFs can be used as stabilizing particles for aqueous foams already at a concentration as low as 5 g/L. The reasons for this are the high aspect ratio which is important for gel formation and the viscoelastic modulus of the air-water interface. Foams stabilized with CNFs are therefore much more stable than foams stabilized by cellulose nanocrystals (CNC). The charge density of the CNFs affects the level of liberation of the CNFs within large CNF aggregates and hence the number of contact points at the interface, and also the gel formation and viscoelastic modulus. The charges also lead to a disjoining pressure related to the long-range repulsive electrostatic interaction between the stabilized bubbles, and this contributes to foam stability.

In the fifth part, the aim was to develop the drying procedure in order to produce a dry porous CNF material using the wet foam as a precursor and to evaluate the dry foam properties. The wet foam was dried in an oven while placed on a liquid-filled porous ceramic frit to preserve and enhance the porous structure in the dried material and prevent the formation of larger cavities and disruptions. The cell structure has been studied by SEM microscopy and APVD (automatic pore volume distribution). The mechanical properties have been studied by a tensile tester (Instron 5566) and the liquid absorption ability with the aid of the APVD-equipment. By changing the charge density of the CNFs it is possible to prepare dry foams with different densities and the lowest density was found to be 6 kg m⁻³ with a porosity of 99.6 %. The Young’s modulus in compression was 50 MPa and the energy absorption was 2340kJ m⁻³ for foams with a density of 200 kg m⁻³. The liquid absorption of the foam with a density of 13 kg m⁻³ is 34 times its own weight. By chemically cross-linking the foam, it was also possible to empty the liquid-filled foams by compression and then to reabsorb the liquid to the same degree with maintained foam integrity. This new processing method also shows great promise for preparing low-density cellulose foams continuously and could be very suitable for industrial up-scaling.

Keywords
Poröst material, cellulosan nanofibriller