

HYDROGELS OF CHIRAL-NEMATIC CELLULOSE NANOCRYSTALS AND NANOCHITIN

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The mechanical strength of hydrogels and aerogels produced from inorganic nano- and microparticles has been out of limits for those based on organic counterparts. Control over the nanoscale architecture of such materials is a possible answer to this challenge, which can even expand properties and functions, including mechano-optical activity. Here we show unprecedented levels of strength by controlling the assembly architecture of cellulose nanocrystals (CNC) and nanochitin (NCh), nanoscaled building blocks presenting anisometry and high intrinsic strength.

High yield (>85%) and low-energy deconstruction of never-dried residual marine biomass is proposed following partial deacetylation and microfluidization. This process results in NCh of ultrahigh axial size that produce highly entangled networks upon pH shift. Viscoelastic and strong hydrogels are formed by ice templating upon freezing and thawing with simultaneous cross-linking. Slow supercooling and ice nucleation at $-20\text{ }^{\circ}\text{C}$ make ice crystals grow slowly and exclude nanochitin and cross-linkers, becoming spatially confined at the interface. At a NCh concentration as low as 0.4 wt %, highly viscoelastic hydrogels are formed, at least an order of magnitude larger compared to those measured for the strongest chitin-derived hydrogels reported so far. The water absorption capacity of the hydrogels reaches a value of 466 g/g. Moreover, our results demonstrate that chiral-nematically ordered hydrogels can lead to aerogels with controlled meso- and microstructures that replicate the liquid crystalline phase transitions of the hydrogels. The obtained architectures are feasible by systematically varying the long-range order of the aqueous CNC dispersions, from mostly isotropic to completely anisotropic. The resultant aerogels display strong coupling between the mesopore fraction and selective light reflection (iridescence) as a function of mechanical load. Specifically, we find that the mechanical performance associated with pore compression under load is greatly enhanced by chiral nematic ordering. These new limits in the mechanical properties of CNC- and NCh-based hydrogels and aerogels point to new structural considerations for the synthesis of porous constructs that exploit the inherent long-range order of such unique building blocks.