ABSTRACTS (PH D THESIS)

Optically transparent nanocellulose-reinforced composites via pickering emulsification

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Introduction

Cellulose nanofibers (CNFs), ~15–50-nm-wide semi-crystalline long fibers made up of 3–5-nm-wide nanofibrils of extended cellulose chains, are one of the marvelous materials produced in the plant cell walls. With their strength seven times stronger than steel and an elastic modulus of 100–130 GPa (of the crystalline part called cellulose nanocrystals, CNCs; 70–90% of the CNF), CNFs not only support the huge body of a tree, but also offer an incredible potential as the reinforcement material for man-made nanocomposites. Also, CNFs have a very high thermal-dimensional stability (coefficient of thermal expansion, CTE: 0.1 ppm K^{-1}), and therefore, are expected to reduce the high thermal expansion of the polymers. However, the processing of CNF-reinforced nanocomposites suffers from the difficulty of dispersing native hydrophilic CNFs in a hydrophobic resin matrix (most resins are hydrophobic). Therefore, many surface modification techniques have been employed to produce hydrophobic CNFs, which made the composite fabrication process long. To defeat this difficulty, previously, a simple impregnation (IM) method has been developed to produce nanocomposite by impregnating hydrophobic resin into a nanopaper of the native (non-modified) CNFs. The resulting nanocomposites were several times stronger, stiffer, and thermal-dimensionally stable than the neat polymer. Additionally, because the width of the CNFs is much less than the visible wavelength, the use of a transparent flexible polymer yielded a transparent and flexible nanocomposite. This transparent nanocomposite caught attention as a substrate for flexible optoelectronic devices due the desirable combination of flexibility and low-CTE. However, it was found that the impregnation process is only limited to produce flat nanocomposites, i.e., three-dimensionally (3D)-molded transparent materials are not obtainable. This is because of the high stiffness of the nanopaper bestowed by intensive hydrogen bonding among the CNFs. Therefore, many exciting applications of the CNF-reinforced transparent nanomaterials, such as the substrate for smart contact-lenses and 3D-curved displays, could not be realized.

Aimed to address the above issues, in this study a very simple water-based method was devised by exploiting the idea of emulsification of oil and water. The dual role of the nanocelluloses as the Pickering-stabilizer of the resin-in-water emulsion and the resin reinforcing nano-component was utilized.

Development of pickering emulsification method for facile fabrication of transparent and 3D-molded CNF-reinforced nanocomposites

The detailed development of the facile Pickering emulsification method to obtain novel transparent materials reinforced with native CNFs was presented. In this method, an acrylic resin-in-water Pickering emulsion (PE) stabilized solely by CNFs was successfully prepared by vigorously agitating in a blender. Because of the strong encapsulation of the liquid resin micro-droplets by the CNFs network, the emulsion could be easily dehydrated by vacuum-filtration and subsequently hot-pressed with a negligible loss of resin followed by UV-polymerization to obtain CNF-reinforced transparent materials. The optical transparency of the nanocomposites was as high as 89% at 16 wt% CNFs content, which indicated that a good dispersion of the network of hydrophilic CNFs in a hydrophobic resin can be achieved via PE method without any chemical intervention. Interestingly, the nanocomposites had a unique self-assembled two-tier hierarchical architecture resulted from the aggregation of the CNF-encapsulated resin micro-droplets during dehydration of the emulsion. Because of the hierarchical structure of the nanocomposites, they possessed a rare but desirable combination of high strength, toughness, and mechanical flexibility compared to their counterparts having a similar CNFs content prepared via the IM method. Also, PEs of

various formulations were prepared by only changing the water content while keeping the CNF-to-resin ratio same, which resulted in the emulsions having different resin droplet sizes. It was found that the PEs with smaller sized droplets produced nanocomposites with high mechanical properties owing to the more uniform hierarchical microstructure. However, the optical transparency was similar for all the nanocomposites irrespective of the resin droplet size.

Meanwhile, because of the inclusion of liquid resin micro-droplets in the CNF-network, which also reduced the H-bonding among the nanofibrils, the nanocomposites could easily be molded into 3D-shaped transparent materials during the hot-pressing. Such a 3D molded transparent material could not be achieved via IM method. The surface of the nanocomposites could even be nano- or micro-molded easily by simple hot-pressing.

Conclusions

A simple Pickering emulsification method to prepare nanocomposites of immiscible nanocelluloses and resins was devised. The potential of this new method in order to fabricate structurally hierarchical, highly transparent, strong, tough, super thermally-stable, and macro/micro/nano-moldable nanocomposites of hydrophilic 'native' nanocelluloses and hydrophobic resins for application in the next-generation optical devices was explored. The super thermal stability of the nanocomposites could allow their application in the devices those frequently undergo extreme changes in the temperature. The successful fabrication of 3D-molded transparent nanocomposites could open new application areas of the nanocellulose reinforced materials. Example of the application could be the substrate for micro-electronic contact lens devices, substrate for curved and flexible displays, data storage devices, microlens arrays for high-resolution 3D-imaging, or anti-reflection substrate for the improved light-trapping in a thin-film solar cell.

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Publications

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