
RECENT RESEARCH ACTIVITIES

UV grafting: surface modification of cellulose nanofibers

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Polymer grafting provides cellulose nanofibers (CNFs) with new features. However, the process of polymer grafting, which generally involves a large amount of organic solvent, is environmentally unfriendly.

In the 1970s, ultraviolet (UV) irradiation was used to generate radicals on the surfaces of cotton cellulose fabric in neutral aqueous conditions, initiating graft polymerization without an external initiator. This method is called UV grafting. Subsequently, UV grafting has been reported in native cellulose from the yellow poplar, cellulose derivatives, and lignocellulose fibers.

CNFs have a much higher specific surface area than cotton fabrics, and hemicellulose has a similar photochemical behavior to cellulose. Therefore, UV grafting is expected to be an effective means of grafting polymer from the surfaces of CNFs. In the current study, we try to utilize the UV to generate radicals on CNFs in aqueous conditions, aiming to graft polymers on CNFs with an organic solvent-free process. We present the new features of polymer grafted CNFs and confirm the versatility of UV grafting by using various vinyl monomers.

We placed a CNF aqueous suspension and the monomer in a Schlenk tube (Figure 1). This was followed by non-strict deoxygenation by bubbling nitrogen gas. We then irradiated the suspension with a UV lamp at constant temperature and stirring speed at a maximum wavelength of 365 nm. As a result, poly (methyl methacrylate) (PMMA) was readily grafted from the CNFs, without destroying the crystalline region of cellulose. As well as PMMA, various other polymers can be grafted from CNFs without using organic solvents.

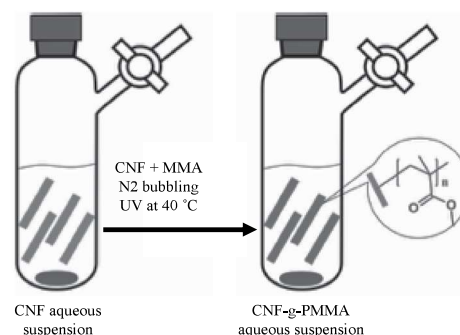


Figure 1. Grafting PMMA from surfaces of CNFs using UV radiation.

The CNFs dispersed well in water owing to their hydrophilic surfaces. Increased hydrophobicity resulted in the aggregation of CNF-g-PMMA in water. After drying and re-dispersing in DMF, we observed severe aggregation of the raw CNFs. On the other hand, CNF-g-PMMA re-dispersed readily in DMF. The water contact angles (CAs) of the CNF-g-PMMA film were $99.7 \pm 0.7^\circ$, much larger than the CA of the raw CNFs. It should be noted that the CAs of CNF-g-PMMA films were higher than the intrinsic CA of PMMA (around 70°), which arose from the roughness generated by hot pressing. The aggregation of CNF-g-PMMA in water and the re-dispersibility of dried CNF-g-PMMA in an organic solvent might facilitate dewatering for storage and supply of CNF materials. Increased hydrophobicity might also improve the compatibility of the CNFs with a hydrophobic matrix.

Surprisingly, CNF-g-PMMA had a unique nanofiber–nanoparticle structure in water. We assume that the primary free radicals were generated on the surfaces of CNFs and that the polymerization process of PMMA was similar to soap-free emulsion polymerization. Our green process may provide CNF materials with new advantages. For example, the aggregation of CNF-g-PMMA in water facilitated the dewatering process, which is important for storage and supply of CNF materials. We can use polymer grafted CNFs in the form of powders owing to their redispersibility after drying. Furthermore, the versatility of UV grafting can improve the compatibility between CNFs and various polymer matrixes.

We believe that this technique, called UV grafting, may provide a greener method for producing CNF materials with novel features.