

Fabrication of self-reinforced cellulose composites

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Cellulose fibers from agricultural waste are used to prepare composites with improved mechanical properties.

In recent years, cellulose fibers have attracted an increasing amount of attention as a potential reinforcement material in composites. Cellulose fibers are an attractive alternative to glass fibers in these cases because they offer several advantages, including biodegradability, sustainability, non-toxicity, and low cost.^{1,2} Poor interfacial interactions between the matrix and the reinforcement materials when cellulose fibers are used in composites, however, is a major problem.

In the preparation of self-reinforced composites (all-cellulose composites), a specific solvent—such as lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc)—or an ionic solvent is used to convert the outer layer of cellulose into matrix material. Meanwhile, the unchanged solid remnants of the cellulose are left to act as reinforcements for the composite.^{3–6} In self-reinforced composites, because both the matrix and reinforcements are cellulose, the interaction between the two is not an issue. Moreover, these composites can be fully recyclable. Although self-reinforced cellulose composites have previously been prepared from various cellulose sources (e.g., cotton, bacterial cellulose, and ramie fibers),^{3,7,8} few studies have so far been conducted in which the composites are prepared from agricultural wastes.

The aim of our work, therefore, was to study the effect of dissolution times on the mechanical properties of self-reinforced cellulose composites that were prepared from agricultural waste (pineapple leaf microfibrils).⁹ To prepare these self-reinforced cellulose composites, we used the surface selective dissolution method. In this process, mats of pineapple leaf microfibrils were immersed in a mixed solution of LiCl and DMAc for 30, 60, 90, and 120 minutes. The composites were then washed with fresh water and subsequently dried in an oven.

We found that after the cellulose fibers were introduced into the LiCl/DMAc solution, the outer part of the cellulose fibers was transformed into matrix material that covered the remaining part of the fibers (see Figure 1). With the longer dissolution times, the amount of matrix material increased and the size of the remaining fibers correspondingly decreased. In addition, we found that the newly formed matrix material

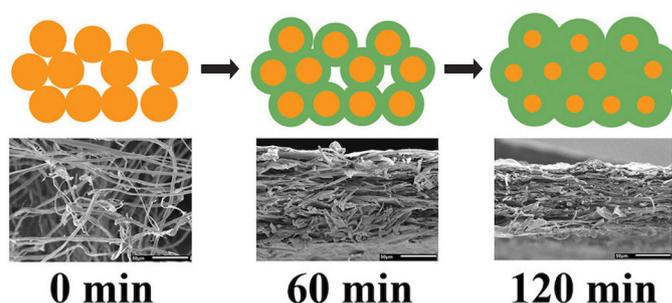


Figure 1. Top: Schematic illustration of the surface selective dissolution method, where orange denotes the unaltered part of the cellulose fibers and green denotes the cellulose matrix. Bottom: Scanning electron microscope images of the fractured surfaces of the cellulose mats (scale bars indicate 50 μm). These samples were immersed in a mixed solution of lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) for 0, 60, and 120 minutes, after tensile deformation.

covered the voids or pores between neighboring fibers. The fractured surfaces of the composites also show that when the dissolution time was longer, more of the voids between the fibers disappeared. We have thus demonstrated that our preparation method successfully changed the structure of the material from a cellulose mat to a cellulose composite.

We examined how the failure mechanism of our composites changed with the variation in dissolution time. For the undissolved cellulose mats, we observed a fiber pull-out deformation mode. We found, however, that the failure deformation changed to that of fiber breakage after 120 minutes of dissolution.

We then studied the effect of the dissolution time on the crystallinity and thermal stability of the composites (see Figure 2). Our results indicate that the degree of crystallinity decreased with longer dissolution times, i.e., the degree of crystallinity of the cellulose mat was about 90%, but decreased to about 65% and then 58% after dissolution for 30 and 120 minutes, respectively. Moreover, our degradation temperature results show a similar trend. We found that the degradation temperature of the undissolved cellulose mat was 371°C, which decreased to 347°C when the mat was dissolved in the solution for 30 minutes. For

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dissolution times of more than 30 minutes, the degradation temperature of the composites decreased slightly. Both our degree of crystallinity and our degradation temperature results therefore indicate a rapid formation of the matrix from the outer part of the cellulose fibers at the start of dissolution, but a slower rate of transformation after 30 minutes.

We have also measured the mechanical properties of our composites as a function of the dissolution time. Stress–strain curves for the composites that were dissolved for 0, 30, 60, 90, and 120 minutes are shown in Figure 3. These results indicate that the tensile strength and modulus of the undissolved cellulose mats were 1.5MPa and 0.1GPa, respectively. In comparison, the composites that were dissolved for 30 minutes exhibited a strength of 7.5MPa and a modulus of 0.4GPa. In addition, we find that the tensile strength and modulus of the composites increased considerably with even longer dissolution times. Indeed, after a 120 minute dissolution time, the strength and modulus of the composites reached 42.8MPa and 1.2GPa, respectively. Similarly, the strain at break also improved with longer dissolution times. These improvements to the mechanical properties of the composites are caused by the larger amounts of the matrix material that cover the pores between the fibers and thus connect adjacent fibers.

In summary, we have investigated the possibility of preparing self-reinforced cellulose composites from pineapple leaf microfibers, and have studied the effect of dissolution time on the properties of the composites. Upon introduction of cellulose fibers into a mixed solution of LiCl and DMAc, the outer part of the fibers dissolved and was transformed into the cellulose matrix that covered the remaining solid cellulose reinforcement fibers. This transformation considerably improved the mechanical properties of the composites, but caused their degree of crystallinity and thermal degradation properties to decrease. With this successful demonstration of self-reinforced composites with

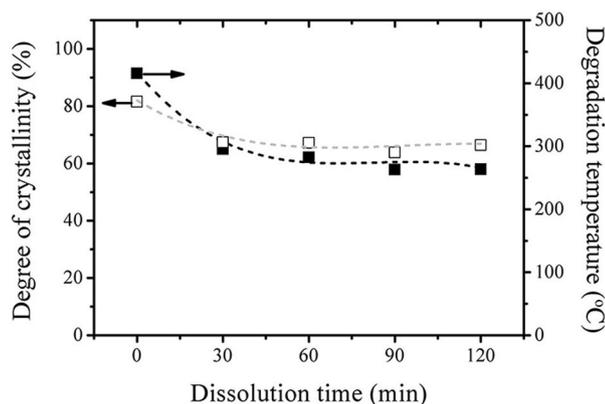


Figure 2. Degree of crystallinity (black squares) and degradation temperature (white squares) of the cellulose mats as a function of dissolution time in the mixed LiCl/DMAc solution.

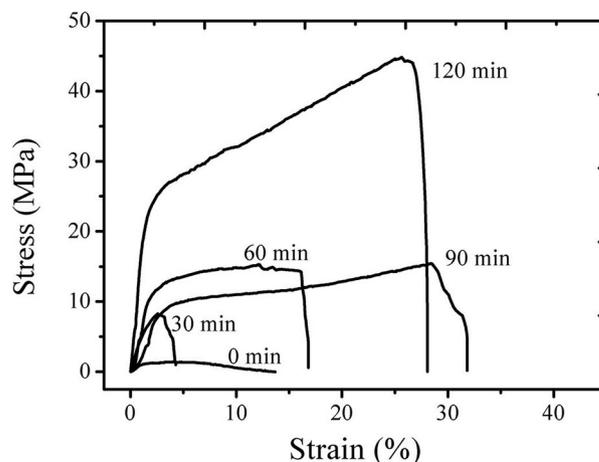


Figure 3. Stress–strain curves for the self-reinforced cellulose composites prepared with different dissolution times.

improved properties, we can now consider applications of our approach. We are therefore adapting our methodology for the preparation of self-reinforced cellulose hydrogels that could be used for biomedical applications. We also intend to test the mechanical and physical properties of the hydrogels we produce.

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