Magnetic field effect for cellulose nanofiber alignment

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Regenerated cellulose formed into cellulose nanofibers under strong magnetic field and aligned perpendicularly to the magnetic field. Well-aligned microfibrils were found as the exposure time of the magnetic field increased. Better alignment and more crystalline structure of the cellulose resulted in the increased decomposition temperature of the material. X-ray crystallograms showed that crystallinity index of the cellulose increased as the exposure time of the magnetic field increased.


Cellulose and its derivatives are one of the most naturally abundant biomacromolecule and among the most widely employed natural polymers in numerous industrial fields, such as the textile industry,1 packaging materials,2 photographic films,3 pharmaceutical membranes,4 and thermoplastics.5 Compared to conventional use, fabrication of cellulose microfibrils,18 and cellulose triacetate19 by strong magnetic field. Thermogalvanometric analysis (TGA) and x-ray crystallogram were taken for comparison of decomposition temperature and observation of nanofiber structure formation.

The cotton pulp (buckeye) having a high degree of polymerization (4500) was torn into pieces and dried with LiCl in a heating oven at 100 °C. The cotton pulp was mixed with LiCl and anhydrous dimethylacetamide and was dissolved by heating at 155 °C with stirring for 24 h. The solution was cooled to room temperature and stored for one week. The cellulose solution was spin coated onto the silicon wafer. A transparent and smooth cellulose film was obtained.

The magnetic field was applied to the samples using a 7 T horizontal superconducting magnet (Oxford Instruments) as shown in Fig. 1, which is located at the National High Magnetic Field Laboratory, Tallahassee, FL. The magnet is characterized by a 150-mm-diameter through bore. The instrument was controlled such that the magnetic field was regulated at 5.3 T, and the region of magnetic field homogeneity (in terms of magnitude) with ±5% error was approximately 12 cm in the axial direction. The sample was placed in the central location of the bore to ensure homogeneous applied field.

FIG. 1. (Color online) Photograph of 7 T horizontal superconducting magnet with 150 mm diameter bore.

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The cellulose films polled with magnetic field were analyzed using a thin film x-ray diffractometer (X’pert MPD, Philips) and a field emission scanning electron microscope (S-4000, Hitachi). TGA was also performed by thermogravimetry- (TG)-DTA (NETZSCH, STA 409 PC).

Figures 2(a) and 2(b) show surface images of regenerated cellulose films under 120 and 180 min exposure time of the magnetic field, respectively. Since the cellulose has negative diamagnetic anisotropy, the direction of alignment for the cellulose nanofibers is perpendicular to the magnetic field direction. Figure 2(a) shows slight alignment of cellulose nanofibers perpendicular to the magnetic field direction when exposed for 120 min. Figure 2(b) shows highly ordered and aligned cellulose fibers perpendicular to the magnetic field, as more time was provided to allow fiber orientation.

Figure 3 shows the FESEM images of cross sections taken along the [Fig. 3(a)] parallel and [Fig. 3(b)] the perpendicular directions with respect to the magnetic field direction, respectively. Since the cellulose nanofibers are aligned to the magnetic field direction, Fig. 3(a) shows the perpendicular arrangement of the cellulose nanofibers with respect to magnetic field direction. Figure 3(b) shows the layered and aligned cellulose structure parallel to the magnetic field direction.

Sun et al.\textsuperscript{20} reported that purified cellulose had a higher thermal stability than the crude cellulose. The purified cellulose increased crystallinity so as to increase the thermal stability. The effect of cellulose nanofiber alignment induced by the magnetic field was investigated in terms of thermal behavior by taking TGA in the temperature range from room temperature to 600 °C at the rate of 10 °C/min under nitrogen flow. Figure 4 shows the results. The decomposition temperatures were 263, 275, 278, 283, and 305 °C for the samples exposed to the magnetic field for 60, 90, 120, 150, and 180 min, respectively. The decomposition temperature was increased as the duration of applied magnetic field increased. This may be due to the increased crystallinity\textsuperscript{20} by the applied magnetic field.

Figure 5(a) shows the x-ray diffraction profiles of regenerated cellulose under different magnetic field exposure times. These profiles were taken on the perpendicular direction with respect to the magnetic field on the regenerated cellulose. The definition of the (200) plane followed that of...
Cellulose II has a crystalline structure. The microcrystalline part of the cotton cellulose is cellulose I, and the regenerated cellulose is cellulose II.\(^{21}\) Cellulose II has 12.1° (110), 19.8° (1\(\bar{1}\)0), and 22° (200) peaks, while cellulose I has 14.8° (110), 16.3° (1\(\bar{1}\)0), and 22.6° (200). The intensity at the 20.6° peak of the regenerated cellulose increased without changing its position, as the duration of applied magnetic field increased. The crystallinity index increased as the exposure time increased without changing its position, as the exposure time increased. This information may not be sufficient to provide the crystal structure change since the change in peak intensity is small. Figure 5(b) shows the x-ray diffraction profiles of the sample along the perpendicular direction and the magnetic field direction when the exposure time is 180 min. Intensity peaks near 12° and 20° for the perpendicular direction and magnetic field direction were higher than those of the magnetic field direction case. Thus, it is clear that this crystallinity increase is mainly due to the magnetic field.

In summary, the regenerated cellulose formed cellulose nanofibers and aligned perpendicularly to the magnetic field. Longer exposure time of magnetic field resulted better alignment of the nanofibers and increased decomposition temperature of the material. X-ray crystallogram results show that the crystallinity index increased as the exposure time increased.

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FIG. 4. (Color online) TGA graphs for the samples with different exposure times of the magnetic field.

Ref. 16. The (200) plane is parallel to the crystal c-axis. In the x-ray diffraction profiles two crystalline reflections at approximately 12° and 20° represent the (110) and (200) crystalline peaks. X-ray diffraction profiles of microcrystalline cellulose, regenerated cellulose, and regenerated cellulose reinforced using microcrystalline cellulose showed different crystalline structures. The microcrystalline part of the cotton cellulose is cellulose I, and the regenerated cellulose is cellulose II.\(^{21}\) Cellulose II has 12.1° (110), 19.8° (1\(\bar{1}\)0), and 22° (200) peaks, while cellulose I has 14.8° (110), 16.3° (1\(\bar{1}\)0), and 22.6° (200). The intensity at the 20.6° peak of the regenerated cellulose increased without changing its position, as the duration of applied magnetic field increased. The crystalline peak representing (110) of the regenerated cellulose increased and shifted to 12.1°, 12.8°, and 13.1° as the exposure time of the magnetic field increased to 90, 150, and 180 min, respectively. This information may not be sufficient to provide the crystal structure change since the change in peak intensity is small. Figure 5(b) shows the x-ray diffraction profiles of the sample along the perpendicular direction and the magnetic field direction when the exposure time is 180 min. Intensity peaks near 12° and 20° for the perpendicular direction case were higher than those of the magnetic field direction case. Thus, it is clear that this crystallinity increase is mainly due to the magnetic field.

In summary, the regenerated cellulose formed cellulose nanofibers and aligned perpendicularly to the magnetic field. Longer exposure time of magnetic field resulted better alignment of the nanofibers and increased decomposition temperature of the material. X-ray crystallogram results show that the crystallinity index increased as the exposure time increased.

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FIG. 5. X-ray crystalograms for (a) the samples with different exposure times of the magnetic field at the perpendicular direction, and (b) the sample when the exposure time is 180 min along the perpendicular and magnetic field directions as the pristine sample without magnetic field.