SHORT COMMUNICATIONS

Formation of Hydrogen-Bonds between Particles of Fine Cellulose Powder to Yield a Transparent Cellulose Plate

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Cellulose is insoluble in ordinary solvents owing to tight inter- and intramolecular hydrogen-bonds, and its major application has been limited to areas related to paper and rayon. Many chemical and physical modifications of cellulose have been investigated to enhance functionality.[1] We developed biodegradable semi-transparent films from an aqueous suspension of micro-fibrillated cellulose and chitosan in acetic acid.[2–5] Mechanical milling is a simple way to prepare fine cellulose powders, which are expected to exhibit excellent characteristics in specific surface, fluidity and chemical activity. Recently, we patented a new technique for fine-powdering of natural polymer[6] and reported the characteristics of cellulose powder obtained by milling in dry-state under several conditions.[7] This study demonstrates that a new type of transparent cellulose plate is obtained by the formation of hydrogen-bonds between particles of fine-powdered cellulose with a small amount of water during hot-press treatment.

EXPERIMENTAL

CF11 (Whatman) was used as pure fibrous cellulose. Vacuum-dried CF11 was milled in a vibratory ball mill at room temperature to prepare fine powders of cellulose.[7] Water content (Wc) of the obtained cellulose powder was adjusted in a humidity control chamber. The powder (1.0 g) with a Wc value of 0—30 wt% was wrapped in aluminum foil and hot-pressed at 25—180°C under 50—300 MPa for 5 min. The obtained plates of cellulose were characterized on the basis of the crystallinity index (CI) from wide-angle X-ray diffraction pattern,[8] the degree of polymerization (DPv) from the intrinsic viscosities of a Cu-ethylenediamine solution[9, 10] and CP/MAS ^{13}C NMR spectra (Varian UNITY INOVA 400 WB).

RESULTS AND DISCUSSION

Characteristics of original and fine-powdered CF11 are summarized in Table I . The original CF11 has a CI value of 93%, with a crystal structure of the native cellulose I type. The powder sample has a CI value of nearly 0%, *i.e.* amorphous. This suggests that the destruction of inter- and intramolecular hydrogen-bonds required for

the high crystallinity of cellulose molecules in original CF11 probably causes the formation of many activated hydroxyl groups in the powder sample which have the ability to form a new network of hydrogen-bonds. A SEM photograph of fine cellulose powder is shown in Figure 1.

Powders with different Wc values of 0—30 wt% were hot-pressed at 150°C under 200 MPa. A transparent cellulose plate was obtained only in the range of Wc=3—6 wt%. With Wc less than 3 wt%, the resultant plates were still white and powdery. The plate became slightly brown with a Wc=6 wt%, and contracted to form cracks when Wc was more than 10 wt%.

A photograph of the plate obtained by hot-pressing the powder with Wc=3.8 wt% at 150°C under 200 MPa, is shown in Figure 2. The center region receiving the given pressure exhibits good transparency and hardness, as confirmed by the fact that the optical transmittance of the plates (thickness=0.9 mm) is between 2.4% and 3.2 % at 590 nm using a normal UV-VIS spectrometer, comparable with that of a commercial tracing paper (thickness=0.04 mm) of 3.1%. Scanning electron microscopy of the transparent plate (Wc=3.8 wt%) revealed that the

Table I. Characteristics of CF11 and fine-powdered cellulose

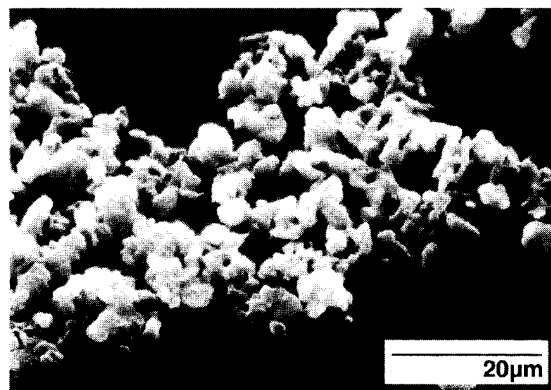|	DPv	CI	Size (shape)
CF11 (original)	220	93	200 μm (fibrous)
Fine-powdered cellulose	155	0	20 μm (particle)

Figure 1. SEM photograph of fine cellulose powders obtained by milling vacuum-dried CF11.
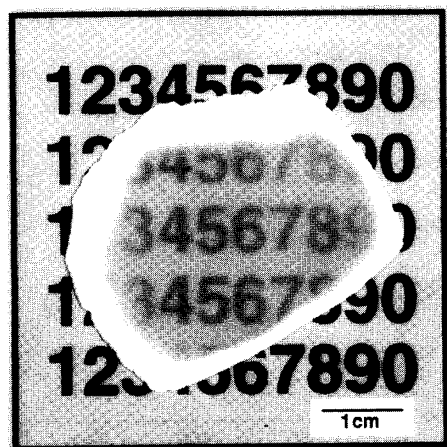

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Figure 2. Photograph of a plate (thickness=0.9 mm) obtained from the powder with Wc=3.8 wt% by hot-press treatment : temperature=150℃ and pressure=200 MPa.

Figure 4. Effects of water content and temperature on CI of the surfaces of the plates : Wc=0 wt% (□); Wc=3.8 wt% (●); Wc= 14.4 wt% (▲).
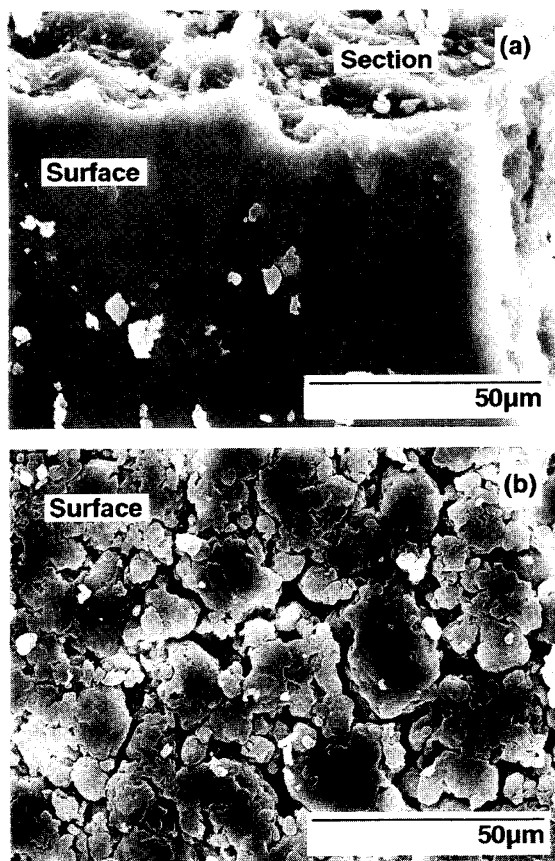

Figure 3. SEM photographs of cellulose plates from powders with Wc=3.8 wt% (a) and Wc=0 wt% (b).

particles of the powder are in close contact without gaps (Figure 3a), in contrast to the case of the plate with a Wc =0 wt% (Figure 3b).

Powders with Wc=3.8 and 5.8 wt% were hot-pressed at different temperatures (25—180℃) under 200 MPa. The plate obtained from the powder with Wc=3.8 wt% at 150℃ had the highest transparency. The plate was still white and powdery at 25℃, and became slightly brown exhibiting a lower transparency at 180℃. With
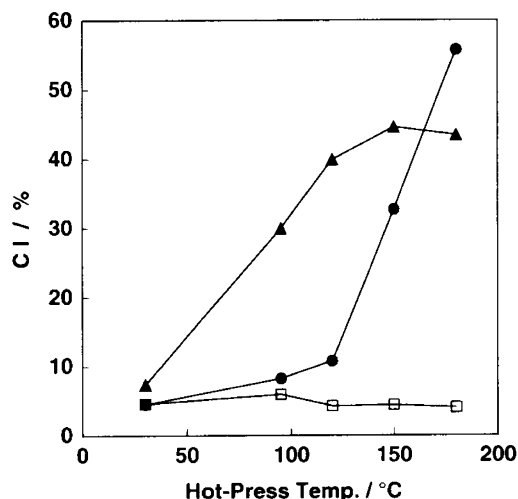
Wc=5.8 wt%, the plate had good transparency at 120℃, but became light brown at 150℃, and contracted to form cracks at 180℃.

To understand factors determining the generation of transparent plates of cellulose described above, we thoroughly examined change in the CI and DPv of cellulose by the hot-press treatment. CIs of the surfaces of the plates obtained from cellulose powders with three different Wc are shown in Figure 4. For the powder with Wc= 0 wt%, which gives a white and opaque plate, CI was not changed by the hot-press treatment at 25—180℃, indicating that cellulose in the plate is still amorphous. For the powder with Wc=3.8 wt%, which gives a transparent plate at 150℃, CI of the plate increased considerably with the hot-press temperature to higher than 120℃. This suggests that the generation of the transparent plate of cellulose is due to change in the crystallinity of cellulose during hot-press treatment. For the powder with Wc=14.4 wt%, which often results in plates with a crack, recrystallization occurs even at the lower temperature, and CI reaches a plateau at a temperature higher than 150℃, probably due to the pyrolysis of cellulose molecules. Further discussion about recrystallization (related to CI) and pyrolysis (related to DPv) appears in other sections.

CF11 (original and powdered) and the plates obtained from the powder with Wc=3.8 wt% under 200 MPa were characterized by solid-state ^{13}C CP/MAS NMR spectroscopy, as shown in Figure 5. The spectrum of CF11 (Figure 5f) has signals assigned to C1, C4, C(2,3,5) and C6 of glucose unit in cellulose molecule.[10, 11] C4 and C6 signals from the crystal phase appear at lower magnetic fields (89 ppm and 66 ppm), while those from the amorphous phase appear at higher fields (85 ppm and 63 ppm). The splitting of the C4 and C6 signals is due to inter- and intramolecular hydrogen-bonding in cellulose.[12, 13] Accordingly, the spectra in Figures 5f and 5a show that original CF11 has high crystallinity, while the fine-powdered CF 11 is amorphous. The signal intensity of C4 and C6 due to crystal phases increased with hot-press temperature, suggesting the recrystallization of cellulose molecules
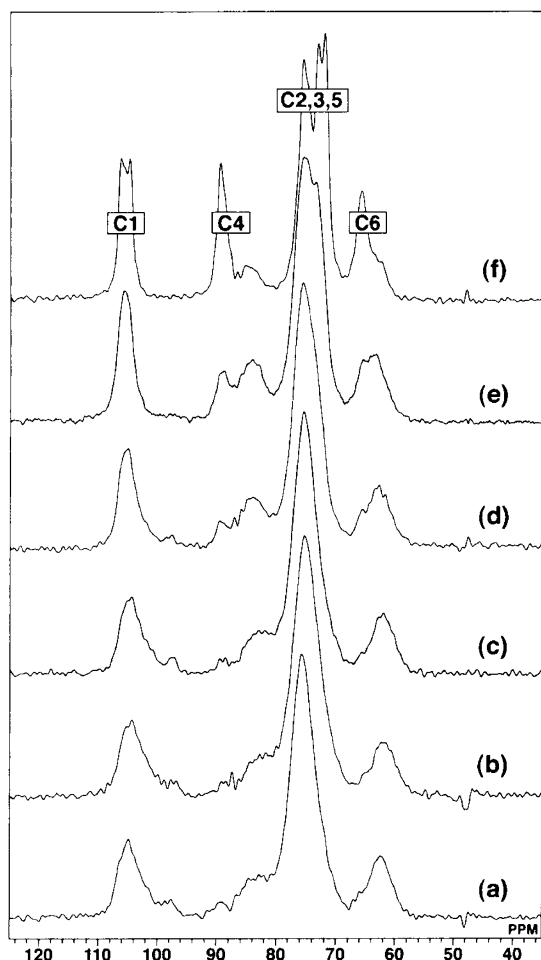
183

Figure 6. Effects of water content and temperature on DPv of the plates : Wc=0 wt% (□) ; Wc=3.8 wt% (●) ; Wc=14.4 wt% (▲).

Figure 5. CP/MAS ^{13}C NMR spectra of the plates : original powder (a) ; hot-press temperatures (℃)=95 (b), 120 (c), 150 (d), and 180 (e) ; original CF11 (f).

through the formation of hydrogen-bonds during the hot-press process.

Figure 6 shows DPvs of the plates obtained from cellulose powders with three different Wc. DPv of the plate from the powder with Wc=0 wt% is a little changed with hot-press treatment. For powders with larger water contents, DPv of the resultant plate significantly decreased more significantly with increase in hot-press temperature, owing to pyrolysis of cellulose molecules. Thus, pyrolysis may cause cracks of the plate.

Changes of DPvs in Wc=3.8 wt% and 14.4 wt% are similar to each other (Figure 6) in spite of large differences in CIs as shown in Figure 4. DPv means an average value for the transparent part of the plate, CI exhibiting a value for the surface of the plate. Thus average CIs of the plates were obtained from X-ray diffractometry of the transparent parts of the plates which were gently ground in a mortar prior to the measurement. Average CIs were lower than surface CIs. For the plate obtained with Wc=3.8 wt% at 150℃ under 200 MPa, surface and average CIs were 33% and 24%, respectively. The difference between them increased with increase in the hot-press temperature. Surface CI depended significantly on pressure. Under 300 MPa, surface CI increased up to 42%, although average CI was still 23%. Recrystallization, thus occurs particularly near the sur-
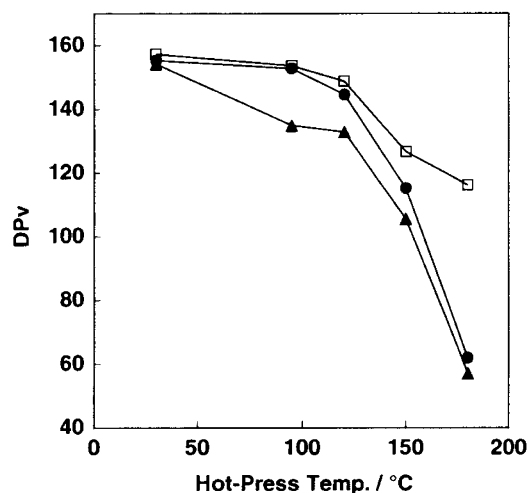
face of the plate, but hardly inside. This implies that DPv in the surface region of the plate differs from that in the inside and accordingly decreases significantly with increase in the hot-press temperature and water content. Thus, in the surface region, recrystallization and pyrolysis of cellulose molecules may proceed because of easy movement of water molecules.

From the above results, we can consider a mechanism for the generation of transparent plates of cellulose by hot-press treatment. Cellulose powder with no water content yields a white and powdery plate but not a transparent one, because of no recrystallization of amorphous cellulose in the hot-pressing. The cellulose powder with Wc=3—6 wt% gives rise to a transparent plate at an appropriate hot-press temperature of 120—150℃, accompanied by recrystallization of the amorphous cellulose. If the same powder is hydrothermally treated in an autoclave at 120℃ for 10 min, the resulting powder does not yield a transparent plate under any hot-press conditions. This powder had CI of *ca.* 40%, suggesting that a network of hydrogen-bonds form principally in each particle, but not between particles of the powder. Accordingly, requirement for the generation of transparent plates of cellulose is the recrystallization of amorphous cellulose during hot-pressing, which induces the formation of a network of hydrogen-bonds even between the particles of the powder. Domain size of the cellulose with DPv=*ca.* 150 in the powder is around 200 nm, and thus the satisfactory contact of particles by such hydrogen-bonds probably allows visible light to pass through the plate regardless of crystallinity. But with further increase in water content of the powder, the plate becomes brown and cracks because of pyrolysis of cellulose molecules.

In amorphous regions of cellulose, some hydroxyl groups have different modes of hydrogen-bonding from those in crystal regions. Water molecules adsorbed by cellulose are bound principally to hydroxyl groups of cellulose molecules in amorphous regions and thus break the hydrogen-bonds there[14,15] and activate the hydroxyl groups. Because the bound water is expected to act as a plasticizer, cellulose may become more mobile. Thus, the
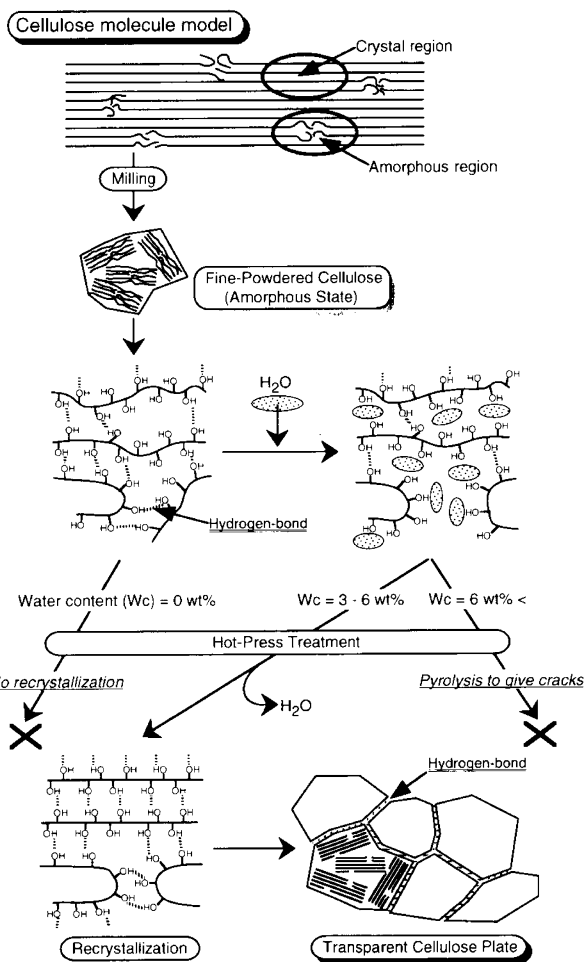
Figure 7. Proposed model for generation of a transparent cellulose plate by hot-press treatment.

Figure 8. Photograph of a transparent cellulose plate (thickness $=ca.\,2$ mm) obtained from the powder (5.0 g, Wc$=3.1$ wt%) by hot-press treatment using a circular metallic-mold : temperature$=$ 150 ℃ ; pressure$=50$ MPa ; hot-pressing time$=20$ min.

formation of a new network of hydrogen-bonds accompanied by removal of water during the hot-press treatment may result in rearrangement and recrystallization of cellulose molecules particularly near the surface of the plate more than in the inner region where water cannot be fully removed. Based on these considerations, we propose a mechanism for generation of transparent plates of cellulose by hot-press treatment as shown in Figure 7.

CONCLUSION

This is the first demonstration of a new type of transparent cellulose plate obtained by the formation of hydrogen-bonds between particles of active fine-powdered (amorphous) cellulose with a small amount of water during hot-press treatment. Hydrogen-bonds are efficiently formed in the specific condition of 3—6 wt% water content and 120—150℃ hot-pressing. Under suit-
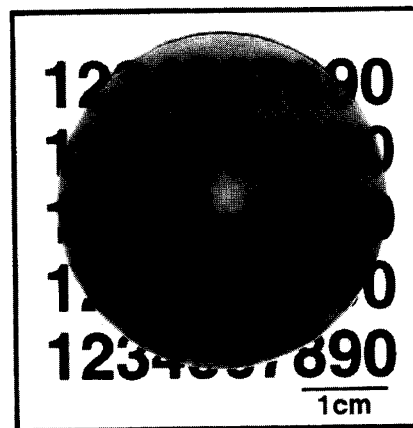
able conditions for the hydrogen-bond formation, a relatively thick transparent plate is obtained (Figure 8).

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