

Production of transparent cellulose plates by hydrogen-bond formation under high pressure

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A new type of transparent plates was prepared from fine-powdered cellulose by hot-press treatment. Hot-press treatment of the powder with a given water content was performed at 150 ° C under 200 MPa for 5 min. The transparent plates were obtained from the powder with 3 - 6 wt% water content (WC). However, the plates were brown and cracked for the WC values more than 10 wt%, having lower transparency for the WC values less than 1 wt%. Recrystallization of cellulose in the plates was confirmed by CP/MAS 13C NMR and X-ray powder diffraction. This recrystallization is probably due to the formation of new hydrogen-bonds in cellulose.

1. INTRODUCTION

Cellulose is one of the most useful biomass polymers and has been used as a raw material for paper, rayon and other products. Cellulose is, however, a stable compound (no thermoplasticity and insolubility in an ordinary solvent) owing to tight inter- and intra-molecular hydrogen-bonds, and its applications have been rather limited. Then we have developed biodegradable films derived from microfibrillated cellulose and chitosan [1-3]. This work describes a new type of transparent plates prepared from fine-powdered cellulose by hot-press treatment. The fine-powdered cellulose was obtained by grinding in a vibratory ball mill [4, 5].

2. EXPERIMENTAL

2.1. PREPARATION OF FINE-POWDERED CELLULOSE

CF11 (Whatman) was used as a pure cellulosic material (> 98 % α -cellulose). Vacuum-dried at 50 ° C for 1 week, CF11 (50 g) was mixed with acetone (10 g) at 50 ° C for 24 h in a sealed mill pot, and then ground in a vibratory ball mill at room temperature.

2.2. MOLDING OF CELLULOSE PLATES

The powder (1.0 g) with a WC value of 0 - 30 wt% was wrapped with aluminum foil. The powder was treated at room temp. to 180 ° C under 50 - 300 MPa for 5 min. The obtained cellulose plates were characterized from their crystallinity index (calculated from X-ray diffraction intensity [6]), degree of polymerization (from the viscosity of Cuen

solution) and chemical structure (with CP/MAS 13C NMR).

3. RESULTS AND DISCUSSION

3.1. FINE-POWDERED CELLULOSE

Characteristics of the prepared fine-powdered cellulose are summarized in Table 1. The crystallinity index (CI) of original CF11 was 93 %, however, the CI value of the powder decreased to nearly 0 % (amorphous cellulose). In the powder state, many inter- and intra-molecular hydrogen-bonds in cellulose were broken to result in many free hydroxyl groups with high ability to hydrogen-bonding.

3.2. THE EFFECT OF WATER CONTENT AND TEMPERATURE

The powder containing 0 - 30 wt% water was hot-pressed at 150 ° C under 200 MPa. The transparent cellulose plate was obtained in the WC values of 3 - 6 wt%. In the cases with the WC values less than 3 wt%, the plates were still white and powdery. On the other hand, the plate was brown in the case with WC = 6 wt%, being contracted and cracked in the cases with the WC values more than 10 wt%. A photography of the plate from the powder containing 3.8 wt% water is shown in Figure 1. Only the center parts received the given pressure. Thus the center parts had transparency and hardness, although the white fringe parts easily broke into pieces. The observation by scanning electron microscopy revealed that the powder particles closely contact

Table 1. Characteristics of the fine-powdered cellulose.

	Shape	Particle size (av.)	CI	DP
CF11(original)	Fibrous	200 μ m (fiber length)	93 %	220
Fine-powdered cellulose	Rugged	20 μ m	0 - 5 %	150 - 170

each other without any gaps in the center parts, different from the fringe parts having many gaps.

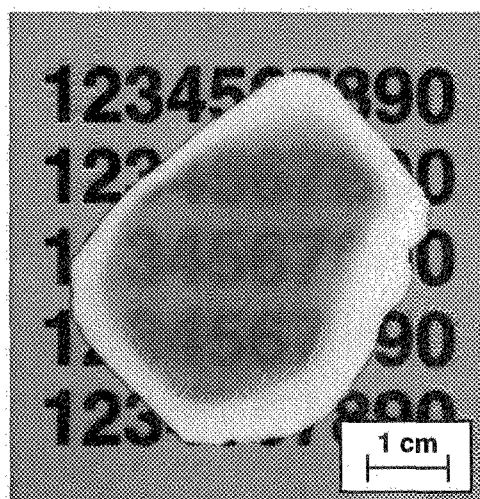


Figure 1. Photograph of the cellulose plate.

The powder was also mixed with MeOH, EtOH, DMAc, DMF or DMSO instead of water. But all the resulted plates had no transparency and were colored brown.

The powder with WC = 3.8 wt% was hot-pressed under 200 MPa at different temperatures (25 - 180 ° C). The resulted plate at 150 ° C has the highest transparency and the largest transparent region. At room temperature, the plate was still white and powdery. At 180 ° C, the plate was colored light brown and its transparency decreased. In the case with WC = 6 wt%, the plate had good transparency at 120 ° C, and colored light brown at 150 ° C. At 180 ° C, the plate contracted and cracked. The cellulose powder with larger water content resulted in the transparent plate at lower temperature.

In Figure 2, the CIs of the surface of the center parts are shown. In the case with WC = 3.8 wt%, the CI value increased with an increase of the hot-press temperature higher than 120 ° C, suggesting that recrystallization of the amorphous cellulose occurred during the hot-press treatment. In the case with WC = 14.4 wt%, the recrystallization occurred even at the

lower temperature. However, the CI value decreased at 180 ° C, probably due to pyrolysis of cellulose molecules. However, the CI value of the plates from the powder with WC = 0 wt% did not exhibit any change from that of the original powder.

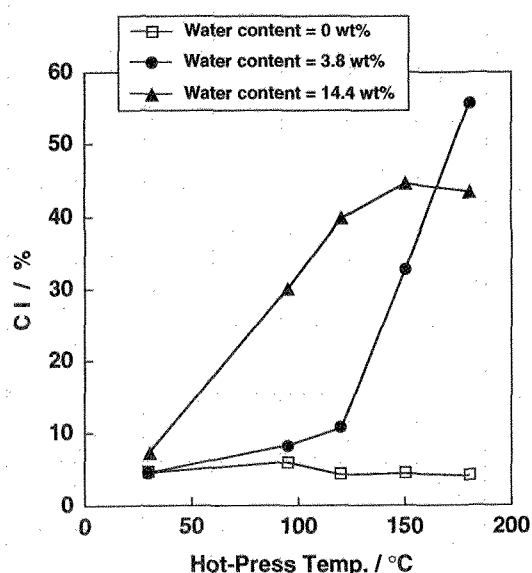


Figure 2. The effects of water content and temperature on CI of the cellulose plates.

Most of water molecules absorbed in the cellulose powder bond to hydroxyl groups of amorphous regions of the cellulose molecules and thus break the hydrogen-bonding [7]. In these cases, the bound water might function as a plasticizer, and molecular chains of cellulose became rather mobile. During the hot-press treatment, removing of water molecules by heating and formation of new hydrogen-bonds probably results in rearrangement and thus recrystallization of cellulose chains. This consideration is consistent with the observation that the powder containing no water could not recrystallize illustrated in Figure 2, and also the fact that amorphous cellulose recrystallized by hydrothermal treatment [8].

The degrees of polymerization of cellulose in the plates are plotted against the hot-press temperature in

Figure 3. With larger water content and higher temperature, the value of the degree of polymerization (DP) significantly decreased owing to pyrolysis of cellulose chains.

In order to confirm that the formation of new hydrogen-bonds between the cellulose particles determines predominantly the generation of the transparent cellulose plate, the cellulose powder with free hydroxyl groups was treated hydrothermally in an autoclave. The treated powder recrystallized with the CI value around 30 %, having little free hydroxyl groups. Thus ability to hydrogen-bonding of this powder is low. The resulting plates showed no transparency under any conditions (water content, temperature and pressure). This insists that the transparent plates were obtained by formation of hydrogen-bonds between cellulose molecules belonging to the different particles.

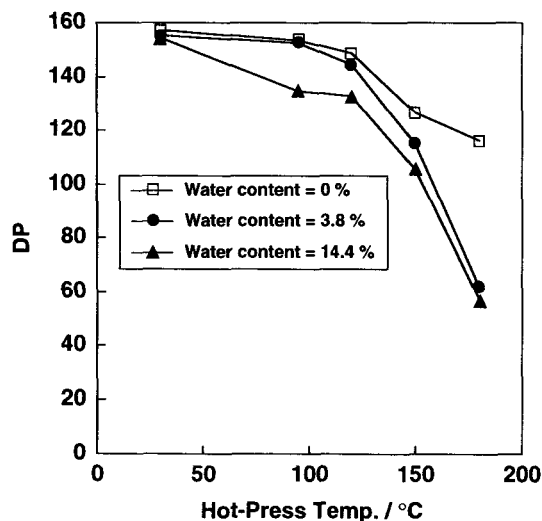


Figure 3. The effects of water content and temperature on DP of the cellulose plates.

3.3. THE EFFECT OF PRESSURE

The powder with WC = 3.8 wt% was hot-pressed under 50 - 300 MPa at 150 °C. In the cases with more than 200 MPa, the resulting plate had transparency. In the cases with less than 100 MPa, the plates had lower transparency and the area of the transparent region became smaller. At less than 50 MPa, the plates were still white and easily broken into pieces.

Figure 4 shows the CI's of the center and fringe parts of the plates obtained under 100, 200 and 300 MPa. The CI values of both the center (surface) and

the fringe part increased with an increase of pressure. The CI value of the center (surface) was more than three times larger than that of the fringe. In Figure 4, center (ground) denotes that the center part of the plate was gently ground in a mortar. The CI values of the center (ground) were lower than those of the center (surface). Further the CI value of the center (ground) did not depend on the pressure. These results show the recrystallization particularly occurred near the surface of the plate, and not so much on the inside.

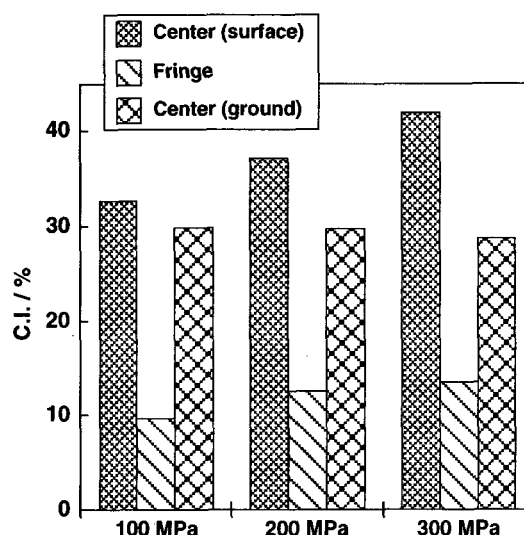


Figure 4. The effects of pressure on CI of the cellulose plates.

A photograph of a transparent cellulose plate obtained with a metallic mold is shown in Figure 5. This plate was prepared from the powder containing 3.1 wt% water under 50 MPa at 120 °C for 20 min.

3.4. SOLID-STATE CP/MAS ¹³C NMR STUDY

The center parts of the plates obtained from the powder containing 3.8 wt% water under 200 MPa and CF11 were measured by CP/MAS ¹³C NMR. The spectra are shown in Figure 6. The spectrum of CF11 has signals well assigned to C1, C4, C[2,3,4] and C6 carbons of glucose unit. With regard to C4 and C6, the signals from crystal phase appear at lower magnetic fields (89 ppm and 66 ppm), those from amorphous phase at higher fields (84 ppm and 62 ppm). Hydrogen-bonds in cellulose are mainly formed between hydroxyl groups and oxygen atoms of glycosidic linkage next to C1 and C4 atoms. The

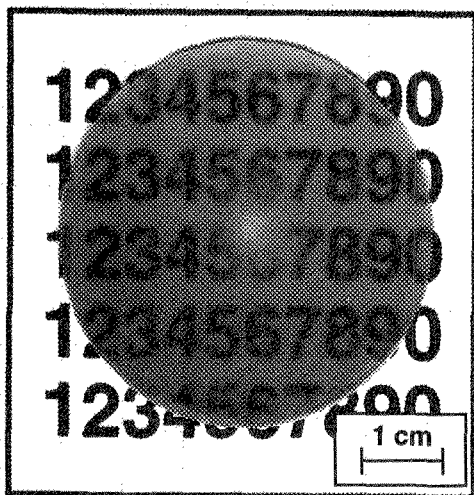


Figure 5. The photograph of the plate obtained with metallic mold.

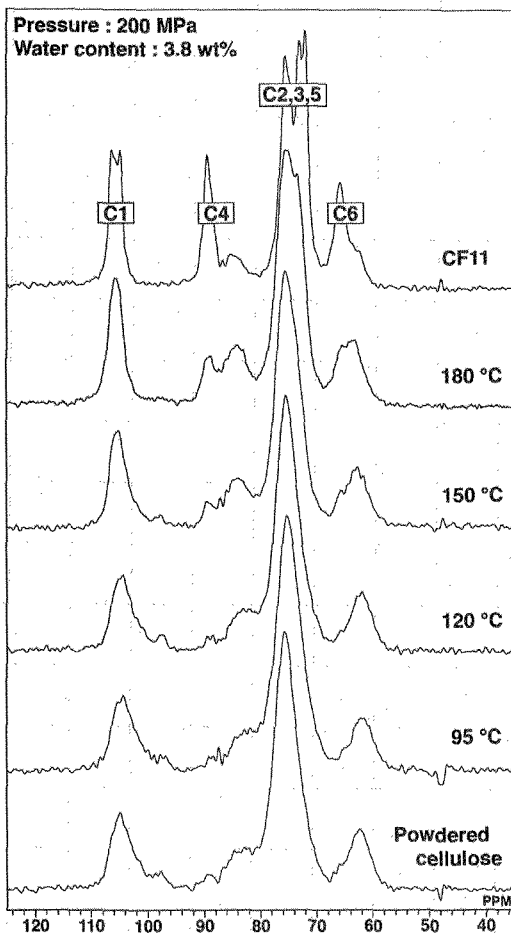


Figure 6. CP/MAS ^{13}C NMR spectra of the cellulose plates.

spectrum of CF11 shows that CF11 has high crystallinity and cellulose I type crystal form. In the spectrum of the fine-powdered cellulose, each signal became broader, and the signals of C4 and C6 at crystal phases disappeared. The CP/MAS ^{13}C NMR spectroscopy confirms that this powder is amorphous. The signal intensities of C4 and C6 from crystal phases increased with an increase of hot-press temperatures. These results also show that recrystallization of amorphous cellulose proceeded accompanied with the formation of new hydrogen-bond, during the hot-press treatment.

4. CONCLUSION

The transparent cellulose plates were prepared from the fine-powdered (amorphous) cellulose containing 3 - 6 wt% water by the hot-press treatment under 50 - 300 MPa at 120 - 150 °C. Even if cellulose is not thermoplastic and insoluble in an ordinary solvent, the fine-powdered cellulose has high ability to hydrogen-bonding. Production of the transparent plates by this method will facilitate intensively new utilization of cellulose.

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