PHYSICAL PROPERTIES OF HANDSHEETS CONTAINING AMORPHOUS CELLULOSE

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ABSTRACT: Mechanical and optical properties of handsheets prepared from mixture of bleached kraft pulp and either microcrystalline cellulose powder (MCP), freeze-dried amorphous cellulose (FAC), or hydrated amorphous cellulose gel (HAC) were studied in terms of crystallinity of the additives and interaction between pulp fibers and the cellulose additives. X-ray diffraction patterns and moisture content of the handsheets showed that both FAC and HAC behaved as amorphous cellulose in handsheets. However, mechanical and optical properties such as Young's modulus, tensile index, tearing resistance, opacity, and scattering coefficients of handsheets showed that MCP and FAC behaved like fillers, and that HAC behaved like strength resins for improving interfiber bonding of pulp fibers. The handsheets had the maximum tensile strength and Young's modulus around 12% HAC content. Effects of the addition of HAC to pulp suspension on physical properties of handsheets seemed to be similar to those of beating of chemical pulp on physical properties of paper. These results and scanning electron micrographs of handsheets indicated that hydrated amorphous cellulose gel can form strong interfiber-bonding with pulp fibers, whereas little interaction is present between pulp fibers and MCP or FAC.

1. INTRODUCTION

Nowadays properties of paper are controlled through various processes in order to respond to various needs of paper and paperboard. Since utilization of recycled pulp has recently been increasing, it became difficult to control paper properties only by selecting pulp quality. Therefore, wet-end is one of the significant processes to control paper properties. No interaction is present between crystalline region of cellulose in pulp and wet-end additives in suspension, but the amorphous region in pulp must have strong interaction with wet-end additives and play a significant role in papermaking.

As reported in previous papers [1,2], a method for preparing new amorphous cellulose, which has stable amorphous structure under aqueous conditions, has been developed. This stability of amorphous structure is significant for model experiments of actual non-crystalline region in cellulosic materials [3]. Then structural changes of cellulose molecules in non-crystalline region during thermal [4], hydrothermal [4], alkaline pulping [5], and acid pulping [6] treatments were studied using new amorphous cellulose samples.

Since the non-crystalline region in pulp must have strong influence on physical properties of paper, even simple addition of amorphous cellulose samples into pulp suspension may improve or control physical properties of paper. In this paper, therefore, handsheets of bleached kraft pulp mixed with microcrystalline cellulose powder, freeze-dried amorphous cellulose, or hydrated amorphous cellulose gel were prepared. Mechanical and optical properties of the handsheets were examined to evaluate effects of the addition of cellulose samples on physical properties, and to elucidate interaction between pulp fibers and the additive cellulose samples. Both freeze-dried amorphous cellulose and hydrated amorphous cellulose gel have stable amorphous structure, as reported previously [1].

2. EXPERIMENTAL

2.1 Samples

Avicel (microcrystalline cellulose powder, Asahi Chemical, Co. Ltd.) was used as a cellulose sample. Commercial bleached kraft pulp made from soft-wood
was beaten using a PFI mill to prepare pulp having 500 mL of Canadian Standard Freeness, and fine fraction (150 mesh-pass) was removed.

Amorphous cellulose was prepared from Avicel, according to the method reported previously [1,2]. The regenerated and hydrated cellulose gel was converted to fine gel particles using a blender, and this fine hydrated gel was kept in water and was used as an amorphous cellulose gel sample. A freeze-dried sample of amorphous cellulose was obtained from the gel sample by freeze-drying.

Handsheets containing bleached kraft pulp and either microcrystalline cellulose powder (MCP), freeze-dried amorphous cellulose (FAC), or hydrated amorphous cellulose gel (HAC) were prepared according to TAPPI Test Methods [7], and were conditioned at 20 °C and 65% relative humidity for more than 1 day. Before the addition of FAC to the suspension of bleached kraft pulp, FAC was soaked in water at room temperature for 2 h to be swollen sufficiently. The retained amounts of the cellulose additives in hand sheets were obtained from basis weight of hand sheets mixed with and without the cellulose additives.

2.2 Measurements

For X-ray analysis of hand sheets, they were shredded and formed to disk pellets. X-ray diffraction patterns of pellet samples were recorded on a JEOL JDX-5B diffractometer equipped with a reflection type goniometer, using Ni-filtered CuKα radiation. Irradiation conditions were 30 kV and 25 mA, and the scanning rate was 1°/min of the diffraction angle 2θ.

Moisture content of the conditioned hand sheets was obtained by the equation (1).

\[ \text{Moisture content (\%)} = \frac{W_{\text{con}} - W_{\text{dry}}}{W_{\text{con}}} \times 100 \]  

(1)

Where, \( W_{\text{con}} \) is weight of the conditioned hand sheets, and \( W_{\text{dry}} \) is weight of the hand sheet dried at 105 °C for 3 h.

Densities and Young’s moduli of hand sheets were obtained for conditioned samples.

Dynamic Young’s moduli of hand sheets were recorded using a Dynamic Modulus Tester PPM-5R (H. M. Morgan Co. Ltd.).

Tensile UTM-III-100 (Toyo Baldwin Co. Ltd.) was used to obtain strain-stress curves of the samples. The specimen size was 15 × ca. 120 mm, and test conditions were: 20 kg load cell, 10 mm/min measuring speed, and 100 mm span length. Tensile strength was expressed as tensile index (N · m/g). Elongation (%) at the breaking point of specimens was also obtained.

Tearing resistances were measured using an Elmdorf tester according to the procedure reported in TAPPI Test Methods [8], and were expressed as tearing index (N · m²/g) [8].

Fig. 1. Optical micrographs of cellulose suspension in water. (A): Microcrystalline cellulose powder. (B): freeze-dried amorphous cellulose, and (C): hydrated amorphous cellulose gel (C).
Reflectivity of infinite pile of handsheets ($R_o$) and reflectance of single handsheet backed by black body ($R_w$) were obtained using a Hunter reflectometer with a green filter. Printing opacities, specific absorption coefficients ($K'$), and specific scattering coefficients ($S'$) of handsheets were calculated from these values and basis weight ($W$, g/m²) of handsheets [9, 10]. Brightness was measured on the Hunter reflectometer with a blue filter [11].

JEOL JEM-35CX was used for obtaining scanning electron micrographs of handsheets.

3. RESULTS AND DISCUSSION

3.1 General Observation

Fig. 1 shows optical micrographs of cellulose samples added to pulp suspension. Microcrystalline cellulose powder (MCP) had a non-swelling form in water, owing to its high crystallinity. Freeze-dried amorphous cellulose (FAC) and hydrated amorphous cellulose gel (HAC) had heterogeneous form. HAC particles swelled much more than FAC in water, even though both FAC and HAC had amorphous structure.

The amounts of MCP, FAC, and HAC retained in handsheets were 68 - 70, 88 - 90, and 92 - 94%, respectively. Since FAC and HAC swelled in water more than MCP, the density of these samples must be far lower than that of MCP. Thus, the amorphous samples have sedimentation velocity in water lower than that of MCP, and this must lead to higher amounts of retention for amorphous cellulose samples in handsheets.

X-ray diffraction patterns of pellet samples of handsheets showed that crystallinity increased with MCP content and decreased with FAC or HAC content. X-ray diffraction patterns of handsheets containing FAC are shown in Fig. 2. These patterns were identical to those of the handsheets containing HAC. The relationships between crystallinity of cellulose I in handsheets and amounts of the cellulose additives were almost linear for all samples, when the 110 peak was used for calculation of crystallinity index [12].

Fig. 3 shows moisture contents of conditioned handsheets of bleached kraft pulp mixed with microcrystalline cellulose powder (□), freeze-dried amorphous cellulose (△), or hydrated amorphous cellulose gel (○). Measured after being conditioned at 20°C and 65% relative humidity for more than 1 day.

Fig. 2. X-ray diffraction patterns of handsheets of bleached kraft pulp mixed with freeze-dried amorphous cellulose. Bleached kraft pulp content (dry weight %): (A): 100, (B): 90.3, (C): 81.3, (D): 62.4, and (E): 42.8.

Fig. 3. Moisture content of handsheets of bleached kraft pulp mixed with microcrystalline cellulose powder (□), freeze-dried amorphous cellulose (△), or hydrated amorphous cellulose gel (○). Measured after being conditioned at 20°C and 65% relative humidity for more than 1 day.

The handsheets containing FAC or HAC had almost identical relationship between moisture content and either FAC or HAC content, and moisture content was increased linearly with FAC or HAC content. After FAC and HAC in handsheets were dried and conditioned, these amorphous celluloses had
3.2 Mechanical Properties

Fig. 4 shows densities and dynamic Young’s moduli of conditioned handsheets. Density decreased with MCP or FAC content, and increased slightly by adding HAC to pulp fibers. This observation indicates that porosity of handsheets is diminished by adding HAC to pulp, and that porosity increases with FAC or MCP content. Thus, FAC and MCP behaved like inorganic fillers in handsheets, whereas HAC did like dry-strength resins for increasing interfiber bonding of pulp fibers. The relationships between dynamic Young’s moduli of handsheets and FAC or MCP content corresponded well to those between density and FAC or MCP content. Handsheets containing HAC had the maximum value of dynamic Young’s modulus around 12% HAC content. This result shows that HAC itself does not play a role in increasing Young’s modulus of handsheets, but some interaction between HAC and pulp fibers around 12 - 25% HAC content must lead to the increase in Young’s modulus.

Tensile indexes and elongations of handsheets were shown in Fig. 5. These values decreased with FAC or MCP content, and this observation also shows that neither FAC nor MCP plays a role in increasing or keeping interfiber bonding of bleached kraft pulp in handsheets. On the other hand, the addition of HAC to pulp contributed to an increase in tensile indexes, and the maximum value appeared around 12 - 25% HAC content. Fig. 6 shows modified tensile indexes of handsheets to express the indexes with constant amounts of bleached kraft pulp, as described in the following formula:

$$MTI = \frac{TI}{(1 - 0.01 \times \text{additive cellulose content} \%)},$$

where TI is tensile index and MTI is the modified tensile index. This figure clearly supports the idea that only HAC contributes to increase in tensile in-
3.2 Mechanical Properties

Tensile energy absorptions (TEA) of samples were also calculated from strain-stress curves (13), and the results were almost identical to those of tensile indexes for all samples. Thus, the addition of HAC can increase interfiber bonding of pulp fibers in handsheets around 12 - 25% HAC content, and HAC plays a role in increasing both elasticity and plasticity of handsheets.

Fig. 7 shows tearing indexes of handsheets. It is known that tearing index has strong relation to the number of fibers in a sheet (14). This relation was applicable to the observation of tearing indexes of handsheets containing FAC or MCP, and these values decreased linearly with FAC or MCP content. In the case of handsheets containing HAC, tearing indexes increased slightly at 3% HAC content and then decreased linearly with HAC content.

These relationships between mechanical properties and HAC content are similar to those between mechanical properties of sheets and beating of chemical pulp.

3.3 Optical Properties

Printing opacities and brightness of handsheets were shown in Fig. 8. Since bleached kraft pulp, MCP, FAC, and HAC have almost equal brightness, all handsheets had almost equal brightness. Printing opacities of handsheets containing FAC were constant for 0 - 57% FAC content, and opacities of FAC in handsheets were identical to that of bleached kraft pulp.

Fig. 8. Printing opacity (——) and brightness (-----) of handsheets of bleached kraft pulp mixed with microcrystalline cellulose powder (□), freeze-dried amorphous cellulose (△), or hydrated amorphous cellulose gel (○).

Printing opacities of handsheets slightly increased with MCP content, because crystalline MCP may have an effect similar to that of inorganic fillers. The addition of HAC to pulp brought about a clear decrease in opacity. This fact shows that HAC plays a role in increasing interfiber bonding of pulp fibers (15). This relationship between opacity and HAC content are similar to that between opacity and beating time of chemical pulp.

Fig. 9 shows specific absorption coefficients (K') and specific scattering coefficients (S') of handsheets. It is known that scattering coefficients have linear re-
Scanning electron micrographs of handsheets of bleached kraft pulp mixed with microcrystalline cellulose powder (A), freeze-dried amorphous cellulose (B), and hydrated amorphous cellulose gel (C).
beating time of chemical pulp. Probably, the swollen and hydrated amorphous cellulose gel, and the swollen and beaten non-crystalline region of chemical pulp have some common points. However, the former case is just the physical addition of amorphous cellulose gel to chemical pulp, and the latter must be more complicated.

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