Mechanical and Dynamic Mechanical Properties of Sheets Made from Micro-Fibrillated Cellulose and Cationic Polyacrylamide

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Abstract: A diluted micro-fibrillated cellulose (MFC) dispersion with cationic polyacrylamide (C-PAM) aq. solution was casted and dried as a plausible model material of fiber-to-fiber bonds in paper containing C-PAM. Mechanical and dynamic mechanical properties of the MFC/C-PAM mixture sheets (MFC/C-PAM sheets) obtained were studied, comparing with those of papers containing C-PAM. The high density and Young's modulus of the MFC/C-PAM sheet, which was twice those of the paper without C-PAM, suggested higher consolidation and fully developed fibril-fibril bonds due to the quite small dimensions of MFC. A significant decrease in scattering coefficient of the MFC/C-PAM sheets accompanied by an increase of C-PAM content suggested that almost all of the C-PAM in the MFC/C-PAM sheets could locate surrounding fibril-fibril bonds. Tensile strength of MFC/C-PAM sheet was far larger than that of the paper without C-PAM. However, the strength increment of the MFC/C-PAM sheets with increasing C-PAM content was smaller than that expected from the difference of Young's modulus between MFC/C-PAM sheets and the papers containing C-PAM, partly because C-PAM itself is brittle. The dynamic mechanical properties of the MFC/C-PAM sheets were, on the whole, similar to those of the paper containing C-PAM, suggesting that the role of C-PAM on the mechanical property (or bonding) was minimal and the most of it was derived from fibril-fibril (hydrogen) bonding in the MFC/C-PAM sheets. Measurement of (dynamic) mechanical properties of the sheets consisted of MFC and various water soluble polymers could be used to evaluate the effects of the polymers on mechanical properties of papers when the polymers were used as dry strength agents.

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1. Introduction

In the last decade the manufacturing and application of so-called cellulose nano-fiber (CNF) or micro-fibrillated cellulose (MFC) have been extensively investigated^{1,2)}. MFC was initially prepared through mechanical pressure-drop homogenization³⁾, and then chemical pre-treatment methods, such as TEMPO oxidation, were developed to reduce the required energy cost⁴⁾. Although various applications of MFC were proposed, composite material with polymer has been a leading commercial application. However, a poor distribution (agglomeration) of MFC has been an unavoidable problem in its application, due to a lack of affinity between cellulose and polymers. Among numerous commercially available polymers, polyacrylamide polymer (PAM) has been used for a long time as a dry strength resin in paper materials. This means that PAM possesses good affinity with cellulose and thus

a mixture sheet of MFC and PAM was recently developed⁵⁾. In the previous studies on cationic PAM (C-PAM) as a paper additive⁶⁻⁸⁾, the effects of addition of C-PAM and its distribution within a fiber wall or paper sheet on strength properties of papers were investigated in order to understand the mechanism of dry strength development of paper containing C-PAM. The results suggested that C-PAM played a role to enhance bond strength per unit bonded area between fibers as well as increasing the bonded area in some extent. Both led to an increase in paper strength⁶⁾. Furthermore, the C-PAM distributed on and/or nearby the surface of fibers particularly affected the development of paper strength^{7,8)}. Pulp fiber used in papermaking is constituted of cellulose micro fibrils as a bundle of CNF or MFC, and thus C-PAM is adsorbed onto micro and nano fibrils extending from wet pulp fibers when C-PAM is added into the pulp slurry. After drying, a somewhat homogenous mixture of C-PAM and nano fibrils could be formed nearby fiber-to-fiber bonds. The mixture may affect mechanical properties of the fiber-to-fiber bonds and further strength

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properties of the resulting paper. Conversely, properties of the nano fibril/C-PAM mixed sheets could be expected to reflect the properties of fiber-to-fiber bonds in paper containing C-PAM⁹⁾.

In this study, sheets were made from mixtures of a commercially available MFC and a cationic C-PAM as a sort of model of fiber-to-fiber bonds in paper rather than a model sheet of a homogenous mixture of polymer and MFC. And its mechanical and dynamic mechanical properties were investigated, comparing with those of paper containing C-PAM.

2. Experimental

2.1 Materials

A commercially available MFC (CELISH KY-100G, Daicel Chemical Industries, Ltd., Japan) was used without further purification. The C-PAM used in this study was referred to a previous report⁷⁾. MFC was diluted to 1% concentration on mass with de-ionized water as well as C-PAM. MFC dispersion was continuously stirred for 2 hrs before mixing with C-PAM. MFC and C-PAM were mixed at given ratios (MFC/C-PAM = 100/0, 99/1, 98/2, 97/3, 95/5 on mass as solid). Thereafter, the mixture was continuously stirred for 30 min before casting into stainless steel molds in order to avoid the flocculation, and storing at room temperature for two days to yield dry sheets. The visually uniform semi-transparent sheets were obtained, irrespective of C-PAM content. Basis weight of the sheets was ca. 30 g/m².

Papers containing C-PAM were prepared from beaten (CSF 510 ml) hardwood bleached kraft pulp and the previously described C-PAM by an internal application method⁷⁾. Total C-PAM content retained in the papers was determined by nitrogen analysis^{7,8)}.

2.2 Measurement of fundamental properties of sheets and papers

As fundamental mechanical properties, tensile strength and Young's modulus were measured under strict condition of in-plane loading, according to the previous report⁷⁾. Thickness for the determination of sheet density and Young's modulus was measured by the rubber platen method according to TAPPI test method T-551. Measurement of optical reflectance of specimens and calculation of scattering coefficient were referred to the previous report⁷⁾.

2.3 Measurement of dynamic mechanical properties of sheets and papers¹⁰⁾

Dynamic mechanical analysis (DMA) was conducted under nitrogen gas flow with Dynamic

Mechanical Spectrometer (DMS 6100, Seiko Instruments, Tokyo, Japan). The measurement was performed using oscillation mode at frequency of 10 Hz and a heating rate of 3 °C/min with the temperature ranging from 120 to 300 °C to determine the dynamic storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta = E''/E'$). In order to measure these under linear viscoelasticity, 10 μ m and 50 mN were selected as the dynamic oscillation amplitude and static tension, respectively. The test specimens were in rectangular shape with dimensions of 30 mm in length of span and 10 mm in width. In this experiment, the temperature was retained at a range from 100 to 120 °C for about 10 min before starting a measurement. Hence, it was not necessary to consider an influence of water content on the mechanical properties.

Table 1 Fundamental properties of MFC/C-PAM sheets and papers containing C-PAM.

Sample	C-PAM content %	Density kg/m ³	Scattering coefficient m ² /kg	Tensile index N·m/g	Young's modulus GPa	Stretch at break %
MFC	0.0	1187	31.3	101	9.9	5.9
	1.0	1296	23.2	118	10.7	5.8
	2.0	1270	20.1	115	10.9	4.5
	3.0	1229	19.7	116	11.6	4.6
	5.0	1217	13.3	97	11.3	4.5
Paper	0.0	671	36.6	55	4.0	4.1
	0.5	671	36.2	70	4.3	4.9
	0.9	682	35.5	84	4.4	5.7
	1.8	695	34.3	87	4.5	5.9

Fig. 1 SEM image of MFC/C-PAM sheet surface.

3. Results and discussion

3.1 Fundamental properties

Fundamental properties of the MFC/C-PAM sheets and papers containing C-PAM are given in Table 1. Density of the MFC/C-PAM sheets was far higher than that of papers and was about twice, irrespective of C-PAM content. Because the dimensions of MFC were essentially quite smaller (according to the information of

the maker : 10-100 nm in width) than those of pulp fibers (ca. 10 μm), the sheets of MFC had higher consolidation than conventional papers, although the former included trunk fibrils with about 1 μm width as shown in Fig.1. Scattering coefficient of the MFC/C-PAM sheets significantly decreased with an increase in C-PAM content. A similar trend of scattering power was reported for latex impregnated papers¹¹⁾. Furthermore, a recent study showed that a higher C-PAM content in MFC/C-PAM sheets gave the high transparency⁵⁾. Generally, scattering coefficient means non-contact surface area surrounding the optically bonded fiber surface in paper, while modulus directly reflects the mechanically bonded fiber surface area which is surrounded by the optically bonded zone. Therefore, the significant decrease in scattering coefficient with increasing C-PAM content for the MFC/C-PAM sheets indicated an increase in the optically bonded area rather than a decrease in the non-contact area. That is to say, most C-PAM in the MFC/C-PAM sheets could locate surrounding fibril-fibril bonds in a similar manner as rubber location surrounding fiber-fiber bonds in latex impregnated papers¹¹⁾.

Young's modulus of MFC sheet without C-PAM was significantly higher than that of papers, suggesting that the increase in mechanical bonded area between fibrils made by refining of fibrous materials was quite large. On the other hand, the increase in modulus with C-PAM content is rather small for both MFC/C-PAM sheets and papers containing C-PAM, as was found in the previous study⁶⁾. Thus, reinforcement of mechanical bonding with C-PAM for both could be caused by the increase in the modulus of the bonding, rather than an increase of mechanically bonded area.

Tensile strength of the MFC/C-PAM sheet without C-PAM was far larger than that of the paper, as expected from both moduli. However the strength increment of the MFC/C-PAM sheets with increasing C-PAM content was smaller than that expected from the difference of Young's modulus between the MFC/C-PAM sheets and the papers containing C-PAM. That is to say, the strength of MFC/C-PAM sheets slightly increased with a further increase of C-PAM, and then rather decreased at the highest level of C-PAM content, while tensile strength of papers containing C-PAM significantly increased with a slight increase in C-PAM content. Taking into consideration that T_g of the C-PAM is ca 217°C (see Fig. 2) and the lower stretch at break of MFC/C-PAM sheets (see Table 1), these results may be derived from brittleness of C-PAM and MFC sheet themselves, thus stress concentration could easily occur in them and the film of

C-PAM was particularly fragile. A change in the shape of test specimen for tensile testing from rectangular to dumbbell shape may be needed for the MFC/C-PAM sheets with higher C- PAM content.

Fig. 2 Temperature dependence of E' (●) and $\tan \delta$ (○) for the MFC/C-PAM sheet : MFC/C-PAM = 95/5 on mass.

3.2 Dynamic mechanical properties

A typical example of the temperature dependence of E' and $\tan \delta$ for the MFC /C-PAM sheet (MFC/C-PAM = 95/5 on mass) is shown in Fig.2. The result was, on the whole, similar to that for the paper containing C-PAM¹⁰⁾, and thus suggested that the role of C-PAM on the mechanical bonding was unexpectedly small and the most of it was derived from fibril-fibril (hydrogen) bonding even in the MFC/C-PAM sheets. The temperature of the $\tan \delta$ peak of the MFC/C-PAM sheet was ca. 217 °C, which agreed with that of a cast film of the corresponding C-PAM. In general, some changes in viscoelastic behavior, such as a shift of $\tan \delta$ peak temperature from that of the original polymer film, were usually detected as a sign of fiber-polymer interaction for paper-polymer composites¹²⁾. The result in this study suggested that a certain interaction between MFC and C-PAM did not exist.

Because characteristic viscoelasticity most clearly appeared in $\tan \delta$ peak, the peak height was calculated by subtracting the value of $\tan \delta$ at 160 °C from the maximum value of $\tan \delta$ around 210 °C for each $\tan \delta$ curve as an index of viscoelastic behavior¹¹⁾. Relations between the peak height of $\tan \delta$ and C- PAM content for the MFC/C-PAM sheets and papers containing C-AM are shown in Fig. 3. In this figure, general trends of the MFC/C-PAM sheets agreed with those of the papers containing C-PAM, suggesting that viscoelastic behavior of the

Fig. 3 Relations between the peak height of $\tan \delta$ and C-PAM content for the MFC/C-PAM sheets and papers containing C-PAM.

MFC/C-PAM sheets should reflect fiber-to-fiber bonds in papers containing C-PAM. That is to say, measurement of (dynamic) mechanical properties of casted sheets consisted of MFC and various water soluble polymers would be valuable to evaluate effects of the polymers on mechanical properties of papers when the polymers were used as dry strength agents.

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