Dynamic Mechanical Properties of Paper Containing a Polyacrylamide Dry-Strength Resin Additive and Its Distribution Within a Fiber Wall: Effect of the Application Method

Ichiro Mihara, Tatsuo Yamauchi

Division of Forest and Biomaterial Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

ABSTRACT: Laboratory handsheets made from lightly beaten hardwood kraft pulp containing various amounts of cationic-type polyacrylamide (PAM) dry-strength resin were prepared by both internal and external application methods. We performed the internal application by adding a dilute aqueous PAM solution to a pulp fiber suspension, whereas we performed the external application by dipping a dry paper (handsheet) into an aqueous PAM solution and further squeezing it out with or without the standard wet press. Attenuated total reflection/Fourier transform infrared analysis combined with a gradual etching method was used to clarify the difference in the depth profiles of PAM within a fiber wall between these application methods. For the internal application method, PAM existed, on the whole, mainly close to the fiber surface and slightly distributed from the fiber surface toward the center of the fiber wall. On the other hand, for the external application method, PAM existed mainly on the fiber surface and around the fiber-to-fiber bonds. Dynamic mechanical properties of the papers containing PAM were measured at temperatures ranging from 100 to 300°C and at the various frequencies. In case of addition by the internal method, no

characteristic viscoelasticity of PAM appeared. On the other hand, external method addition at the nearly same retention level of PAM gave the characteristic viscoelasticity. These findings suggest following things: when cationic-type PAM dry-strength resin was applied by the internal method, the PAM distributes within the fiber wall in a molecularly dispersed state. The induced state of PAM within the fiber wall, with no existence of a phase of PAM, led to the disappearance of the viscoelasticity of the PAM. On the other hand, the external application method brought about the PAM distribution around the fiber-to-fiber bonds and over the fiber surface. The induced state of PAM, the existence of a kind of PAM phase, led to the appearance of the viscoelasticity of the PAM itself. Dynamic mechanical analysis may be a good method for examining whether PAM is molecularly distributed or making aggregates in paper and other polymer composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3836–3842, 2008

Key words: additives; composites; mechanical properties; transitions; viscoelastic properties

INTRODUCTION

In modern papermaking, the use of dry-strength agents such as cationic starch and polyacrylamide (PAM) resin is gradually increasing because of the increased use of hardwood fibers and recycled fibers and the further lowering of the basis weight. As a conventional method, dry-strength agents are included in the paper sheet by the addition of an aqueous solution to the paper stock before its sheet forming (internal application method). However, the direct application of the aqueous solution to a dry paper sheet (external application method), such as in the size pressing method, has recently been investi-

gated[1] because the quality of water for sheet making has been getting worse because of a requirement for closed water cycle systems and also an increase in paper recycling and, thus, decrease in the retention level of the agent. Although the mechanism of strength development by both application methods is not well known,[1–3] the difference in the distributions of agent within a fiber wall between the internal and external application methods could deeply affect the strength development. According to a previous study of paper sheets containing PAM,[1] attenuated total reflection/Fourier transform infrared (ATR–FTIR) analysis combined with the gradual etching method clarified a difference in the depth profile of PAM within a fiber wall between these application methods.[4,5] That is, PAM existed, on the whole, mainly close to the fiber surface and slightly distributed from the fiber surface toward the center of the fiber wall for the internal application method. In contrast, the external application caused PAM to exist mainly

on the fiber surface. To show the effect of the difference in the polymer distribution on the fundamental mechanical properties of paper sheets containing PAM, the dynamic mechanical properties of these sheets prepared by both application methods were measured at temperatures ranging from 100 to 300°C in vibration mode at various frequencies in this study because the dynamic mechanical properties of polymers and their related materials are well known to reflect their fine structure and polymer distribution.[6]

EXPERIMENTAL

Materials

The pulp used in this study was a commercially available bleached hardwood kraft pulp and was screened in advance with a classifier with a 100-mesh screen.[2,4] The fines-free pulp was beaten in a Norway Pulp Paper Research Institute (PFI) mill (standard pulp-refining mill for laboratory paper making) to 550 mL of CSF (quantitative estimation of pulp refining). Aliquots of the pulp slurry were diluted with tap water to a 0.15% concentration, and then, an aqueous solution of the PAM, which was adjusted to a concentration of 0.75%, was added to the pulp slurry in the range 0.5–3 mass % on oven-dry pulp. No other additives, such as alum, were added to the slurry to simplify the experiment. After the addition of PAM, the slurry was allowed to stand at room temperature for 30 min before sheet forming (internal application method). Handsheets (basis weight $\approx$ 60 g/m^2) from the pulp slurry with or without PAM were made according to Technical Association of Pulp and Paper Industry (TAPPI) test method T-205 (the forming of handsheets for physical tests of pulp). That is, wet handsheets were dried with standard drying rings to hinder shrinkage. For internal application, the PAM distribution was quite homogeneous through both the z and x and y directions of the sheet.[4]

We performed the aforementioned external application method by dipping the dry handsheet without PAM into the aqueous PAM solution in a range of PAM concentrations from 0 to 1.5%. After that, the sheets were promptly put on the drying plate and wet-pressed to squeeze out the extra solution with a spongy rubber roller, without the use of the standard wet press. The wet handsheets were air-dried with standard drying rings. For this method, the pressure of rolling was much lower than that of the standard wet press, and the squeezing time was just about 5 s for the roll press, whereas the standard wet press was done for 7 min. Because of insufficient squeezing and drying on the plate, the PAM distribution was rather heterogeneous in the z direction for this method; that is, the PAM concentration at

the upper side of the sheet was more than 100% higher than that at lower side for the sheets containing PAM at concentrations over about 2.0%. A series of paper sheets containing concentrations of PAM from 0 to about 2.5% applied by both application methods were used in this study. Practical external application methods, such as tub sizing, must cause heterogeneous PAM distribution in the z direction. However, to eliminate the heterogeneity in the z direction even in the external application method for more precise comparison between both application methods, we replaced the wet-pressing operation (after the dipping of dry paper into the PAM solution) with a spongy rubber roller by the wet pressing with the standard press. A quite homogeneous PAM distribution in the z direction was eventually obtained despite the use of the external application method.

Additionally, the composite of paper and PAM (paper–PAM composite) was prepared as a replacement of the PAM film because the PAM film was easily broken during the dynamic mechanical measurements under the conditions mentioned later. We made the composite by pouring approximately 10 mL of 3.5% PAM solution onto a base paper held with drying rings and by further keeping it intact during the drying. The PAM content of the composite was approximately 25%.

The PAM used in this study was a commercially available standard cationic PAM (relative molecular mass = 2×10^6, charge density = 0.6 mequiv/g) from Arakawa Chemical Industries Co., Ltd.[4] The PAM content retained in the sheets was determined with the ATR–FTIR spectroscopy method for both application methods.[4] Furthermore, for the external application method, we also calculated the PAM content with the PAM concentration of the solution and the weight increase by weighing the dry handsheet before dipping and the wet handsheet immediately after we squeezed out the extra solution. The PAM content determined by weighing for the external application method was equal to the averaged PAM content at the upper and lower sides, which were determined by the ATR–FTIR method.

Basic properties

As a fundamental mechanical property, tensile strength was measured according to TAPPI test method T-494 (tensile breaking properties of paper and paperboard) with an Instron-type machine (Shimadzu Autograph AGS-100, Kyoto, Japan). The thickness for the determination of sheet density and dynamic mechanical modulus was measured by the rubber platen method according to TAPPI test method T-551 (thickness of paper and paperboard: soft platen method). The fundamental properties of a

TABLE I
Basic Properties of Paper Handsheets Containing PAM Added with Internal and External Application Methods

Retained PAM (%)	Application method	Sheet density (kg/m^3)	Tensile index (kN m/kg)
0	—	648	40
0.7	Internal	690	51
1.1	Internal	689	54
1.4	Internal	739	63
0	External 1	589	30
0.6	External 1	623	40
1.1	External 1	641	43
1.8	External 1	645	62
2.3	External 1	635	77
0.8	External 2	688	59
1.1	External 2	681	65

External method 1 involved wet pressing with a rubber roller; external method 2 involved a standard wet press.

series of the sheets with various retention levels are given in Table I. PAM addition by the internal application method brought about increases in the density and tensile index (the tensile strength is usually expressed as the tensile index in paper industry/science).[2] Further details of the mechanism of strength development by both methods will be provided in an upcoming article.[7]

Depth profile of PAM within the fiber wall (ATR–FTIR analysis combined with sputter etching)

ATR–FTIR analysis with a KRS-5 prism was carried out to determine the retained PAM content. Furthermore, the same analysis after successive sputter etching of the paper sheet was carried out for the depth profiling of the PAM content within the fiber wall.[4] A sample sheet cut in a rectangle 48 × 12.5 mm^2 was dried *in vacuo* for 1 h before argon-gas etching. The sample on the electrode was sputter-etched stepwise from 10 to 75 min in a radio frequency sputtering equipment (RFS-200, Shinku Kiko, Tokyo, Japan) under the following conditions: electric power = 5 W and argon-gas pressure = 100 Pa. The sputtering conditions were selected to bring about homogeneous etching without structural changes (microroughening) on the surface.[8] From the relationship between the etching time and decrease in mass/weight corresponding to the thickness of the removed layer of the paper, it was possible to follow the partial concentration profiles of PAM as a function of distance from the original surface of the fibers.[4]

Dynamic mechanical properties

Dynamic mechanical analysis (DMA) in vibration mode was conducted with a dynamic mechanical spectrometer (DMS210, Seiko Instruments, Tokyo,

Japan) at frequencies from 0.01 to 10 Hz to determine the dynamic storage modulus (E'), loss modulus (E''), and tan δ (E''/E'). To measure these properties under linear viscoelasticity, 10 μm and 0.3 N were selected as the dynamic oscillation amplitude and static tension, respectively. The specimens for DMA tests were rectangular in shape with dimensions of 30 × 10 mm^2. In this experiment, the temperature for beginning the measurements was over 120°C after the sample was heated at 100°C for approximately 10 min and was moved up to 300°C, so it was not necessary to consider the influence of water content in each sample for the mechanical properties.

RESULTS AND DISCUSSION

Depth profile of PAM within a fiber wall

The relation between the PAM content and etching depth is shown in Figure 1 for the sheets made by both application methods at a PAM retention level of approximately 2%. According to the previous study,[4] these curves can be considered a sort of depth profile of PAM within the fiber wall. Generally speaking, the maximum PAM content was placed at the surface, and the content decreased toward the inner side for both application methods. However, some high level of PAM content was still observed at the inner part of the fiber wall for the internal method; in contrast, there was almost no PAM content at the inner part for the external method. On the basis of these findings, schematic drawings of the PAM distribution within and around the fiber wall are shown in Figure 2 for both application methods. (The fiber length of hardwood pulp is on
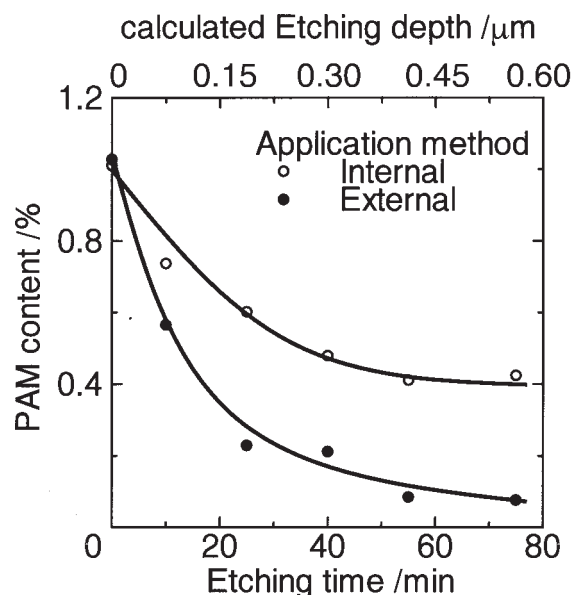

Figure 1 Relation between the PAM content and etching depth for both application methods.
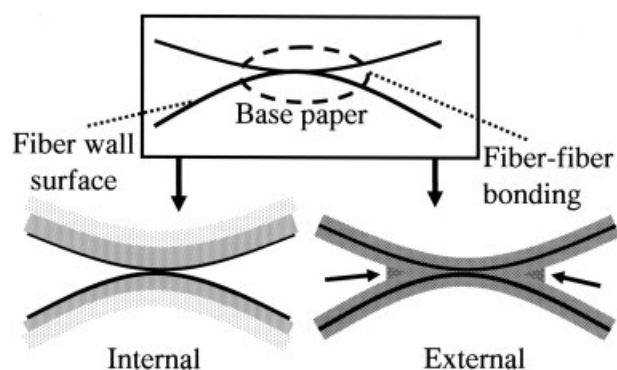
Figure 2 Schematic drawings of the PAM distribution within and around a fiber wall for both application methods.

average ca. 1 mm. If the fiber were compared to a big tree 10 m high, the fiber diameter would be ca. 0.3 m, and the sizes of the fibril and PAM molecule would correspond to a twig and a leaf, respectively.)

Although differences in the PAM distribution and its mechanism will be discussed in detail with the strength development mechanism in a later report,[7] the results may be explained as the PAM molecular adsorption on the external fibrils from fibers in wet conditions and the following collapse of the fibrils on drying.[4] The difference in the PAM distribution between both application methods could arise partly from a difference in the degree of external fibrillation on the fibers between the fiber suspension and wet paper sheets after drying. Furthermore, PAM solution in the paper sheets after wet pressing moved to the space around fiber-to-fiber bonds because of the capillary phenomenon in the external application method. Eventually, the PAM distribution filling the space around the fiber-to-fiber bonds had to be formed.[9]
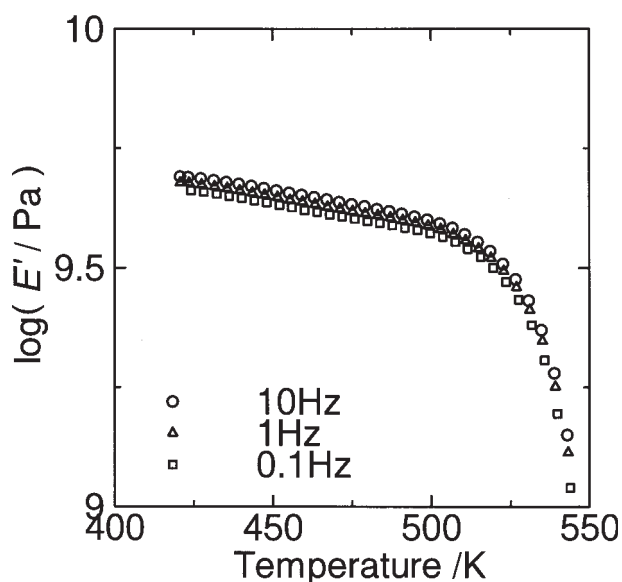
DMA of the base paper and the paper–PAM composite

Because base paper and PAM were the components of the paper sheet with PAM added, it was necessary to examine the results of DMA for the base paper and the paper–PAM composite as a replacement of the PAM film before we could examine the effect of the application method on the DMA of paper with PAM added. The results of DMA for both E' and tan δ are given in Figures 3–6 in the form of temperature dependence: Figures 3 and 4 for the base handsheets and Figures 5 and 6 for the paper–PAM composite.

For any frequency used, E' of the base paper gradually decreased with increasing temperature from the beginning to 520–530 K (ca. 250°C) and then rapidly decreased with increasing temperature at over approximately 530 K, whereas the tan δ remained almost constant with increasing temperature, and a rapid increase in tan δ occurred at over approximately 530 K. The rapid decrease in E' and the increase in tan δ arose from the thermal decomposition of cellulose.

On the other hand, E' of the paper–PAM composite showed a steep drop between about 470 and 500 K, in addition to the gradual decrease shown in the base paper. Furthermore, tan δ showed a clear peak at the same temperature. These changes were clearer at lower frequencies and possibly arose from the quasi glass transition of PAM in the composite. That is, the viscoelasticity of PAM appeared in the temperature dependence of E' and tan δ as an occurrence of the molecular mobility transition of the PAM polymer. A similar viscoelasticity was more clearly observed for latex-impregnated paper as a rubber–paper compo-
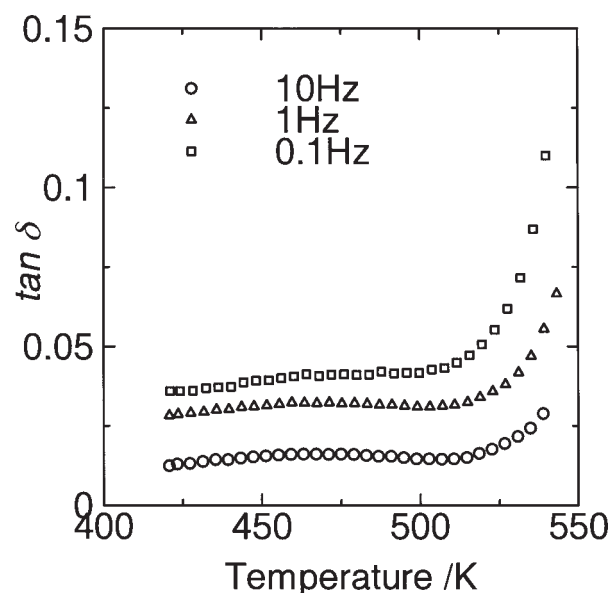

Figure 3 Temperature dependence of E' for the base paper.

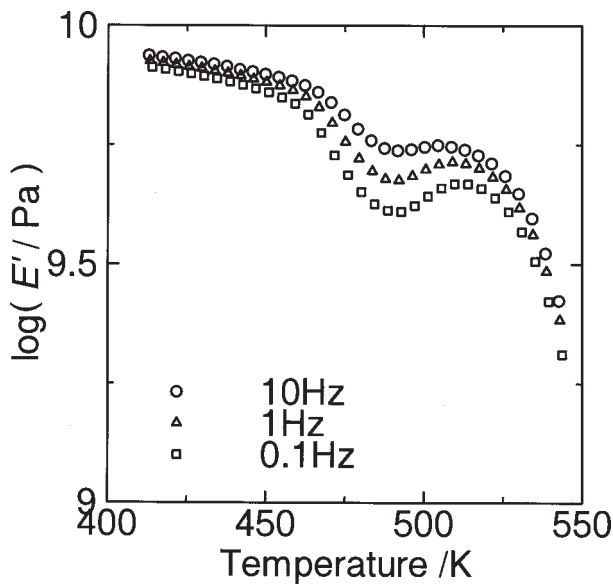**Figure 4** Temperature dependence of tan δ for the base paper.

Figure 5 Temperature dependence of E' for the paper–PAM composite.

sites, where the rubber was distributed around the fiber-to-fiber contacting points, even though the rubber content was approximately 5%.[10]

DMA of the paper containing PAM (comparison of the application method)

The results of DMA for the paper sheets with PAM added for E' and tan δ are given in Figures 7–10 in the form of temperature dependence: Figures 7 and 8 for paper with the internal application method (retained PAM content = 1.4%) and Figures 9 and 10 for paper with the external application method (retained PAM content = 1.8%).
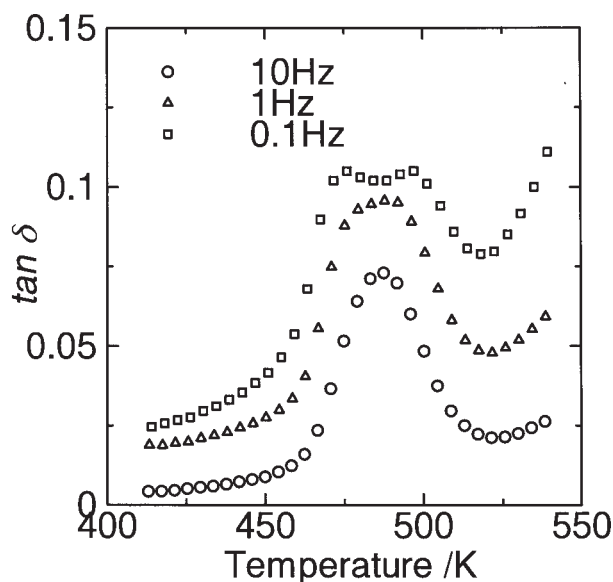
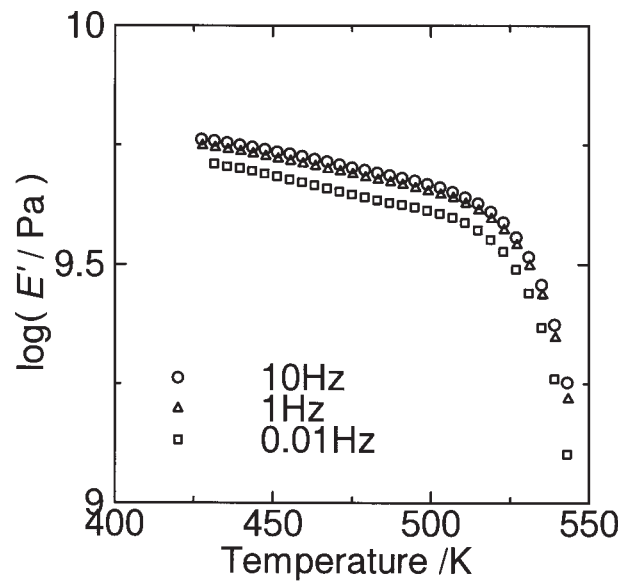**Figure 6** Temperature dependence of tan δ for the paper–PAM composite.

Figure 7 Temperature dependence of E' for paper containing PAM with the internal method (PAM content: 1.4%).

In case of the handsheets containing PAM by internal application, E' decreased linearly, and tan δ was almost constant; then, both changed rapidly above 530 K. These tendencies were exactly same as those of the base paper.

In contrast, the dynamic mechanical behavior of handsheets containing PAM by external application was the same as that for the paper–PAM composite; that is, drops in E' and the peak of tan δ occurred. A remarkable difference in dynamic mechanical behavior was recognized between the internal and external
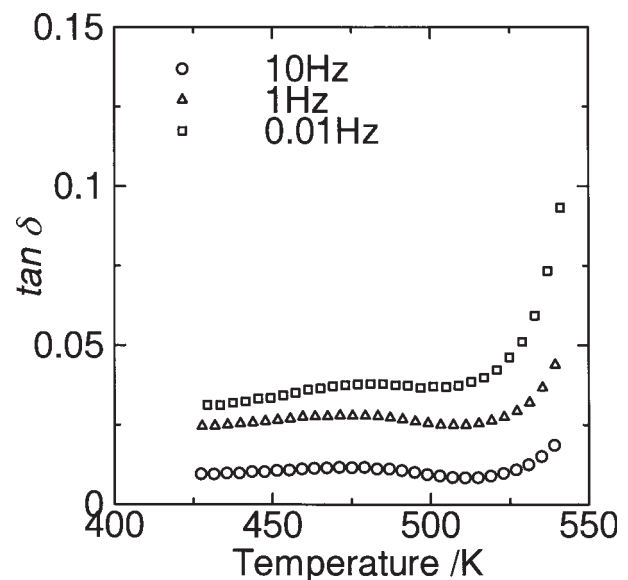

Figure 8 Temperature dependence of tan δ for paper containing PAM with the internal application method (PAM content: 1.4%).
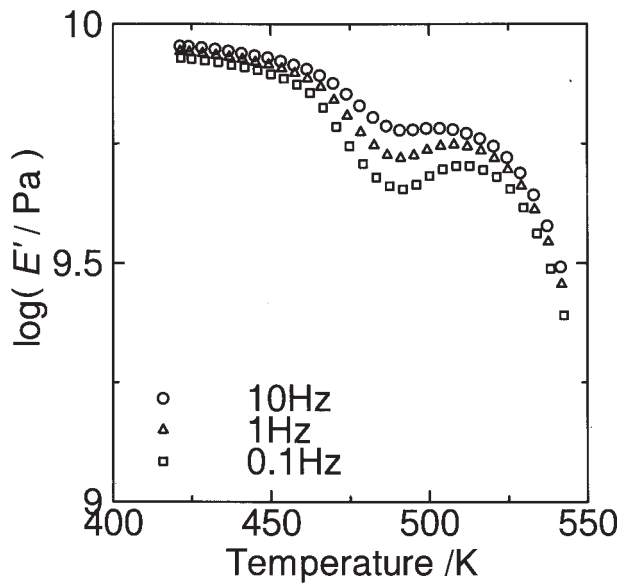
Figure 9 Temperature dependence of E' for paper containing PAM with the external application method (PAM content: 1.8%).
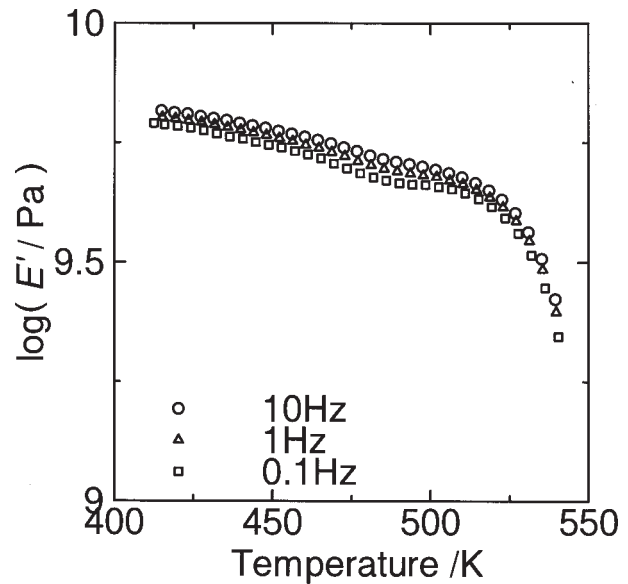

Figure 11 Temperature dependence of E' for paper containing PAM with the homogeneous external application method (PAM content: 1.1%).

application methods, although the PAM content was somewhat higher for the PAM-containing paper with the external application method. The handsheets with PAM added by the external application method gave a heterogeneous tendency in the z direction, as mentioned before. That is, PAM mainly lay to the surface side. The surface layer rich in PAM meant that the vicinity of the paper surface was quite similar to the paper–PAM composite. This is a possible reason the dynamic mechanical properties of the sheet with PAM added by the external

application method were similar to those of the paper–PAM composite.

Effect of the z-directional PAM distribution

It was thought that the heterogeneity in the z-directional PAM distribution could influence the appearance of viscoelasticity. Therefore, the dynamic mechanical properties of the z-directionally homogeneous sheet with PAM added by the external application method (retained PAM content = 1.1%) are shown in Figures 11 and 12.
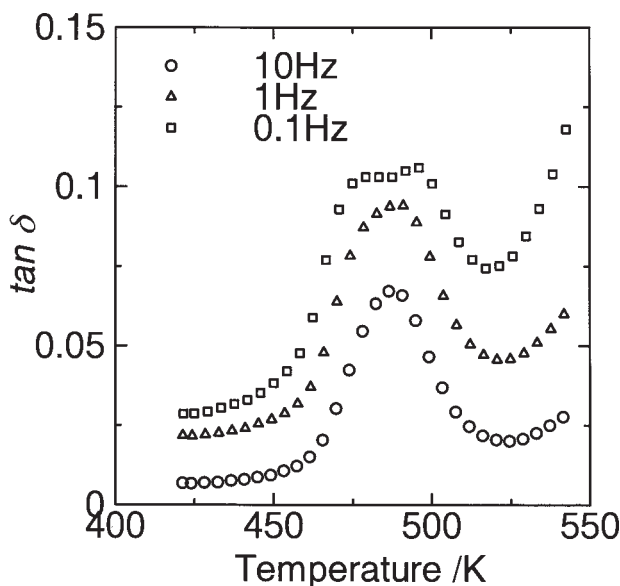

Figure 10 Temperature dependence of tan δ for paper containing PAM with the external application method (PAM content: 1.8%).

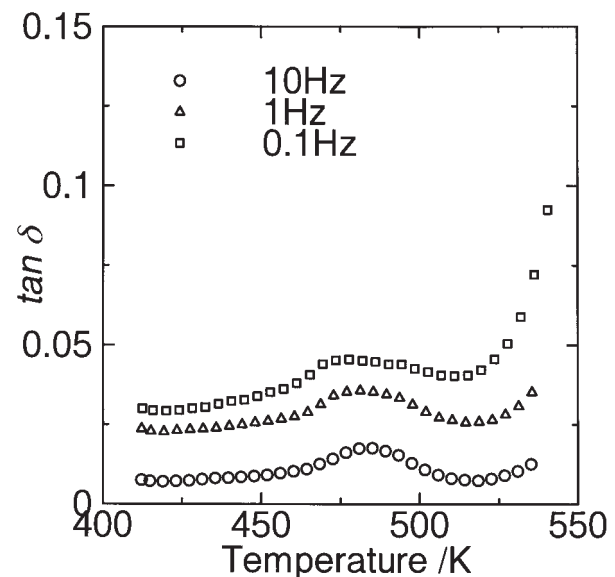**Figure 12** Temperature dependence of tan δ for paper containing PAM with the homogeneous external application method (PAM content: 1.1%).

The characteristic changes showing viscoelasticity in E' and tan δ were rather small, partly because of a lower PAM content. However, the viscoelasticity still appeared in this sheet, and a tan δ peak shift with increasing frequency was also observed. The heterogeneous PAM distribution in the z direction seemed to give a more pronounced viscoelasticity.

Relationship between the viscoelasticity and PAM distribution within the fiber wall

Whether or not PAM in paper displayed its viscoelasticity may have depended on the difference in PAM distribution caused by these application methods. As mentioned before (see Fig. 2), PAM was broadly distributed in the depth direction of the fiber wall, although it was mainly distributed near its surface for the internal application method. In contrast, PAM was distributed near the surface within the fiber wall, around the fiber-to-fiber bonds, and over the surface for the external application method. If one considers that both the fiber itself and the fiber-to-fiber bonds contributed to the transmission of mechanical power and, further, that the PAM around the fiber-to-fiber bonds and over the surface made a continuous PAM phase, the PAM phase could reveal its viscoelasticity. Thus, the viscoelasticity that appeared when the external application method was used may have arisen from the PAM around the fiber-to-fiber bonds and the PAM covering the fiber surface. On the other hand, the PAM in the sheet made with the internal application method may have not made the PAM phase and displayed no viscoelasticity.

The PAM used in this study was not an amphoteric PAM but a cationic PAM, which was molecularly dispersed in the aqueous solution. On application of the cationic PAM into the pulp fiber suspension, it may have been adsorbed molecularly on fibrils projecting from the fiber surface. These fibrils with PAM collapsed on their original fibers during drying.[4] Thus, the PAM may have distributed within the fiber wall in a molecularly dispersed state, with a depth profile as shown before, and may have become a kind of PAM–cellulose composite. Therefore, if the PAM in the aqueous solution had a tendency to aggregate to itself and was adsorbed on the fibrils in the aggregated state, PAM may have made a small continuous PAM phase within the fiber wall, and the viscoelasticity of the PAM could have appeared. DMA of paper made with the internal method with amphoteric PAM, which to some extent has a tendency to aggregate, will be explored in a further study. Furthermore, the relation between the viscoelasticity of a polymer composite and the size of the polymer phase within it is very interesting.

CONCLUSIONS

In case of the cationic-type PAM dry-strength resin application with the internal method, the PAM distributed within the fiber wall in a molecularly dispersed state. In the induced state within the fiber wall, no existence of a PAM phase led to the disappearance of the viscoelasticity of the PAM. On the other hand, the external application method brought about the PAM distribution around the fiber-to-fiber bonds and over the fiber surface. The induced state of PAM, consisting of a PAM phase, led to the appearance of the viscoelasticity of the PAM. DMA was a useful method for examining whether the PAM was molecularly distributed or aggregating in the paper composites.

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