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Thermal-softening properties of water-swollen wood: The relaxation process due to water soluble polysaccharides

YUZO FURUTA, YOSHIHIRO OBATA, KOZO KANAYAMA
E-mail: furuta@nirin.go.jp

To clarify the thermal-softening properties of water-swollen wood, the viscoelastic properties of wood specimens conditioned to various moisture contents and of water solutions of amorphous cellulose, hemicellulose and milled wood lignin, have been studied in the temperature range from −150 to 0°C at frequencies ranging between 0.5 and 10 Hz. A relaxation process around −40°C was observed in wood specimen with high moisture content. It was observed in wood specimens with lower moisture content at higher temperature. The value of apparent activation energy for the relaxation process was 50 kJ/mol. On the other hand, a similar relaxation process was observed in water solutions of amorphous cellulose and hemicellulose around −40°C, but it was not observed in water or water solution of milled wood lignin. The values of apparent activation energy for the relaxation process were 230–545 kJ/mol. Therefore, we considered that the relaxation process was due to the water-swollen polysaccharides and affected by the situations of water molecules. © *2001 Kluwer Academic Publishers*

1. Introduction

At present, there is a lot of knowledge about the thermal-softening behavior of water-swollen wood because many researchers have studied it from many viewpoints. Most of their reports show that only one relaxation process due to the thermal-softening of lignin was observed in the temperature range from room temperature to 100°C [1, 2]. But Hillis *et al*. [3] and Iida [4] observed two relaxation processes in the same temperature range, and they considered that the relaxation processes of the lower and higher temperature ranges were due to hemicellulose and lignin, respectively. As we can realize from these reports of two different types, the effect of hemicellulose on the thermal-softening behavior have not been clarified yet.

On the other hand, for the Udaikamba wood (*Betula maximowicziana*) with about 25% moisture content tested in the tangential direction, we detected a relaxation process around −40°C which has never observed through the measurement in the temperature range from −150 to 0°C. And, we revealed that this relaxation process was not observed for the Udaikamba wood treated with a 15% NaOH water solution, treated using steaming (200 °C, 10 min), or with low moisture content [5]. From these results, we considered that this relaxation process was due to water- swollen hemicellulose [5].

In the present study, for the purpose of the elucidation of the mechanism for the relaxation process around −40°C, the dynamic viscoelastic properties for wood specimens with various moisture contents, and solutions of hemicellulose or other components of wood were measured in the temperature range from −150 to 10°C. In this report, we deliberated the mechanism for this relaxation process.

2. Materials and methods

2.1. Materials

Japanese hinoki (*Chamaecyparis obtusa*) was used. The size of specimen was 60 mm (L = longitudinal direction) by 1.5 mm (R = radial direction) by 4 mm (T = tangential direction). The measurements of the dynamic viscoelastic properties were carried out after the moisture content of the specimen was controlled using constant humidity boxes.

In addition, samples were made from amorphous cellulose (AC), xylan (XA), xyloglucan(XG) and milled coniferous wood lignin (MWL). These samples were dissolved in the water, and these water solutions were used for measurements of the dynamic viscoelastic properties after adjusting the concentrations to about 2–10%. The measurements of the dynamic viscoelastic properties were carried out with the glass fiber filter paper (60 mm (length) × 5 mm (width) × 1.8 mm (thickness), Advantec Co. Ltd., GLASS FIBER FILTER PAPER GA100) impregnated with each water solution of AC, XA, XG or MWL.

2.2. Measurements of the dynamic viscoelastic properties

The temperature dependencies of dynamic elastic modulus (E') and loss modulus (E'') were measured by the tensile forced oscillation method using an automatic dynamic viscoelastometer (Orientec Co. Ltd., Rheovibron DDV—25FP). The measurements were conducted using some constant frequencies over a temperature range from −150–10°C with a programmed heating rate of 2°C/min. The measurement frequencies were 0.5, 1, 2, 5 and 10 Hz, the span was 50 mm and the displacement amplitude was 12 μm. The tensile direction for the wood specimen was the radial direction.

The measurements for the wood specimen moisture content were carried out quickly after taking the specimen out of the constant humidity boxes. The moisture content of the specimen before the dynamic test measurement was almost the same after the measurement.

3. Results

3.1. The dynamic viscoelastic properties of wood in the temperature range below 0°C

Fig. 1 shows the temperature dependencies of E' and E'' at 0.5 Hz for the wood specimen with each moisture content conditioned from 7.1 to 23.9%. With E'', two relaxation processes were observed in the case of 12.9% moisture content and over. So, on increasing the moisture content, each E'' peak temperature shifted towards the lower temperature range and the E'' peak value of each relaxation process was larger. Each relaxation process in the higher temperature range and in the lower temperature range were labeled the α process and the β process, respectively. The relaxation process which was similar to the α process had been detected by mechanical or dielectric measurement, and it was considered due to the motions of methylol groups and adsorbed water molecules [6]. On the other hand, the E'' peak of the α process almost disappeared on extracting hemicellulose from the wood specimen. Consequently, it is certain that hemicellulose in wood is concerned in the α process. Moreover, the E'' peak temperature location and the E'' peak value of the α process were dependent on the moisture content of the specimen, so the α process was largely affected by the amount of adsorbed water molecules.

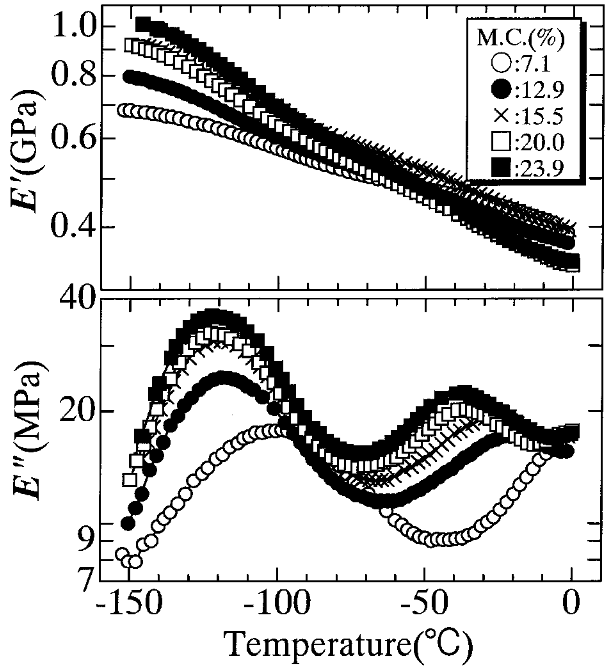

Figure 1 Temperature dependencies of the elastic modulus E' and the loss modulus E'' at 0.5 Hz for wood specimen with various moisture contents (M.C.).

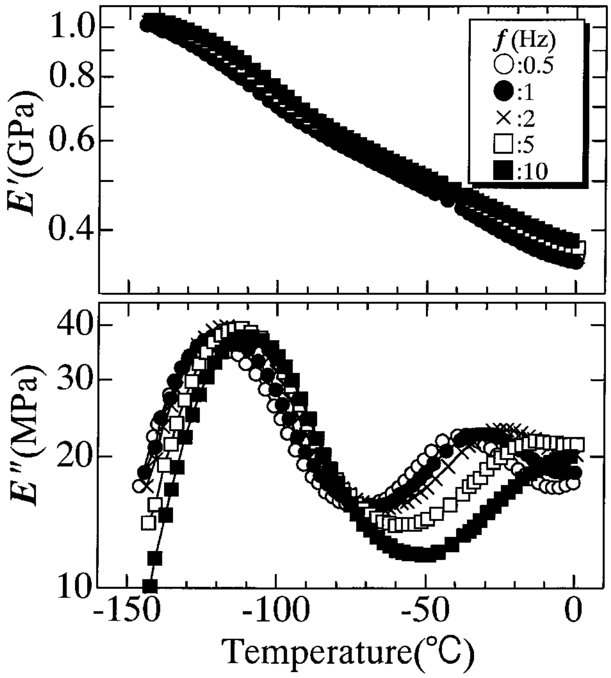

Figure 2 Temperature dependencies of the elastic modulus E' and the loss modulus E'' at 0.5, 1, 2, 5 and 10 Hz for wood specimen with 23.9% moisture content.

Fig. 2 shows the temperature dependencies of E' and E'' at 0.5 to 10 Hz for the wood specimen with 23.9% moisture content. Increasing the measurement frequency, the E'' peak temperature location of the α process shifted to the higher temperature range. From the relationship between the reciprocal of the absolute temperature ($1/T$) for the E'' peak and the logarithmic frequency ($\log f$), we calculated the value of apparent activation energy(ΔE). Fig. 3 shows the relationship

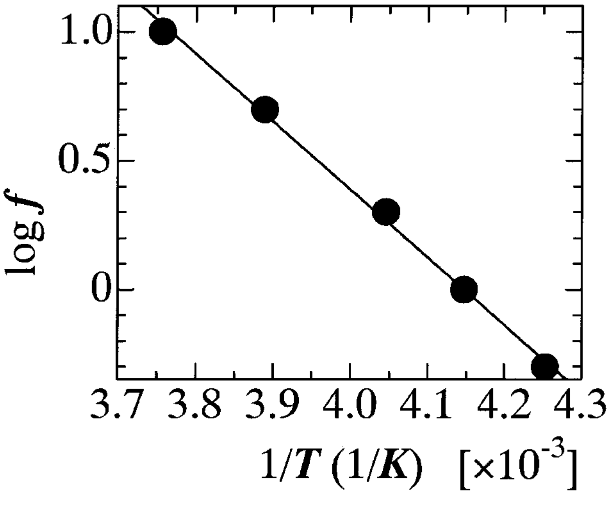

Figure 3 Relationship between logarithm of frequency ($\log f$) at loss maximum and reciprocal of absolute temperature ($1/T$) for wood with 23.9% moisture content.

between 1/T and log f. The value of ΔE is given by the slope of the regression line. The value was about 50 kJ/mol.

This value differed rather from that of Udaikamba wood (about 105 kJ/mol) [5]. This difference might be due to the variation between specimens, but mainly, it might result from relaxation processes existing above 0°C. In the temperature range from 0 to 100°C, the relaxation process due to the thermal softening of lignin was observed, and the properties of the relaxation process were different between hardwood and softwood [7]. Moreover, a temporal relaxation process due to drying or heating history exists in the temperature range lower than that of the thermal softening of lignin, and the loss peak temperature location is changed by the condition of drying or heating [8]. These relaxation processes might interact, and the apparent E'' peak temperature of the α process was shifted towards the higher temperature range. So the values of ΔE in some specimens might differ.

3.2. Temperature dependencies of the dynamic viscoelastic properties for wood components

In this study, the strips of the glass fiber filter paper were used for the support material of the samples because the samples were water solutions. This glass fiber filter paper is composed of short glass fibers, so the value of E' or E'' for this glass fiber filter paper is much smaller than those of the freezing samples. Moreover, we could not detect the relaxation process when the strip of this glass fiber filter paper was measured in the temperature range from −150 to 0°C. It was suggested from these results that the value of E' or E'' for the glass fiber filter paper penetrated with water solution was almost the same value as for the water solution. The real value of E' or E'' for the specimens could not be calculated because the sectional area of the specimens could not be measured exactly. For this reason, the relative E' and the relative E'' normalized with reference to E' and E'' at 100°C were used instead of the real values of E' and E'', respectively.

Fig. 3 shows the temperature dependencies of the relative E' and the relative E'' of AC, XA, XG and MWL solutions at 1 Hz. With the respect to E', water and MWL samples softened at about 0°C, but AC, XA and XG samples softened at about −50°C. With respect to E'', the peak around 120°C was observed in all samples. The location of the peak temperature depended on the measurement frequency. This relaxation process is labeled the β' process because the location of the peak temperature for the β or β' process is almost same. The β' process might be due to water in the water solutions because it was detected not only in the samples of some water solutions but also in the water sample. On the other hand, in the temperature range from −50°C to 10°C, the sharp E'' peak was observed in the water or MWL sample at 0°C. So, in the water solutions of polysaccharides, the clear peak of E'' was observed around −40°C corresponding to the degradation in E'. These results supported the thermal-softening behavior of hemicellulose or lignin in the temperature range from −150°C to 100°C which Back *et al.* expected [9].

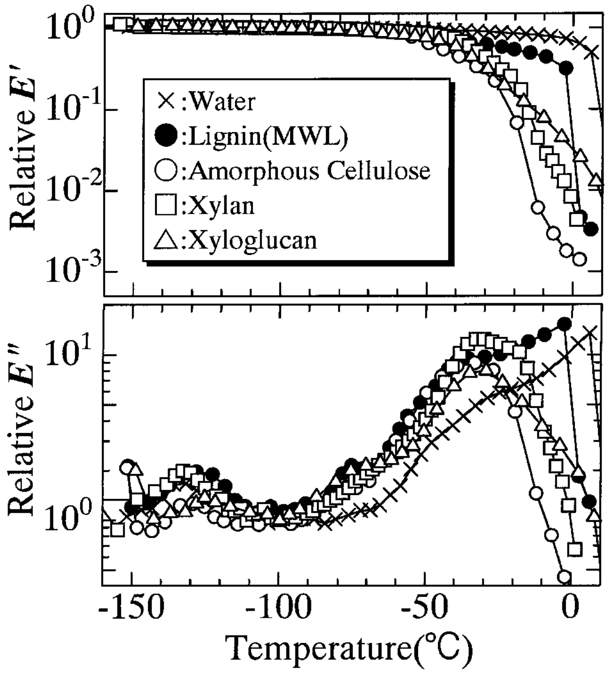

Figure 4 Temperature dependencies of the relative elastic modulus E' and the relative loss modulus E'' at 1 Hz for the solutions of wood components impregnated into the glass fiber filter paper.

The E'' peak around 0°C observed in the water or MWL sample did not depend on the measurement frequency, so it might show the melting of water. On the other hand, the E'' peak around −40°C observed in the water solutions of polysaccharides depended on the measurement frequency. These results might show that this peak around −40°C was due to some relaxation process. This relaxation process was labeled the α' process. By way of parenthesis, the α' process was not observed in the samples of oven-dried amorphous cellulose and hemicellulose. From the relationship between the reciprocal of the absolute temperature (1/T) for the E'' peak and the logarithmic frequency (log f), we calculated values of (ΔE). Fig. 4 shows the relationship between 1/T and log f. The values were 230–545 kJ/mol. The α' process of E'' might correspond to the α process which was observed in wood specimens except for the difference of each ΔE.

4. Discussion

As Fig. 1 shows, the α process at about −40°C due to the water-swollen hemicellulose was observed in the wood specimen with the high moisture content. This relaxation process must be related to the adsorbed water molecules because the location of this peak in E'' depended on the moisture content. On the other hand, as shown in Fig. 3, the α' process, which was similar to the α process, was observed in the water solution of amorphous cellulose or hemicellulose although the thermal-softening behavior of the lignin solution was almost same as that of the water sample. This result suggests that the α process observed in the wood specimen with the high moisture content is due to polysaccharides swollen by the water molecules.

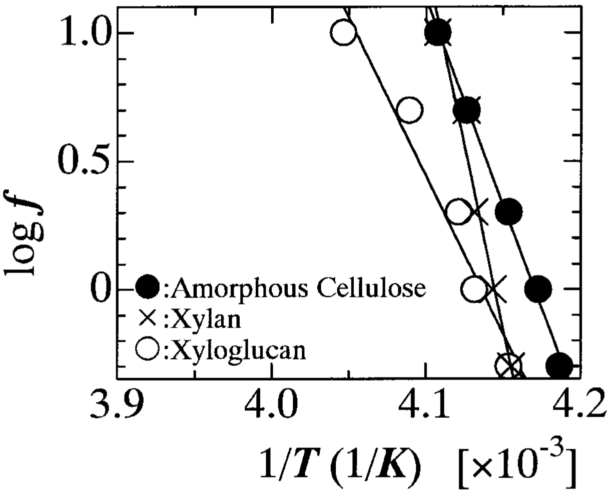

Figure 5 Relationships between logarithm of frequency (log f) at loss maximum and reciprocal of absolute temperature ($1/T$) for the solutions of amorphous cellulose, xylan and xyloglucan.

Since these results were related to water, we need to consider the behavior of water at this temperature range. It is well-known that the behavior of water molecules which exist around high polymer molecules differ from the behavior of bulk water molecules. These water molecules which exist around high polymer molecules were often called "abnormal water" or "non-freezing water". It is well-known that the glass transition of water molecules in a high polymer gel or the glass transition of water molecules cooled quickly was observed around −120°C. Therefore, the β process observed in the wood specimen [6], [10], [11] and the β' process might be caused by water molecules in a high polymer gel. On the other hand, it had been reported that abnormal water molecules around polysaccharides were divided into plural groups because the peak of endothermic reactions was observed in the temperature range from −50 to 0°C when the DSC measurement was carried out for the water solution of mucopolysaccharide [12]. This peak temperature range is almost same for the α process in the wood specimen with the high moisture content or the α' process in the water solution of each polysaccharide.

Obataya *et al.* reported that a relaxation process like the α process was observed in cane specimens with high moisture content, in canes which contained a lot of monosaccharides and disaccharides originally. Moreover, they reported that the relaxation process like the α process was not observed in cane specimens extracted monosaccharides and disaccharides but the relaxation process like the α process was observed in cane specimens impregnated with water solution of grape sugar [13]. Although our results differed from these results reported by Obataya *et al.*, the α process mechanism or the relaxation process like the α process observed in the cane specimen, might be almost same if we considered that these phenomena were caused by water-swollen sugars.

On the other hand, the values of ΔE in wood or in amorphous cellulose or hemicellulose solutions differed obviously (the values of ΔE in wood: 50–105 kJ/mol, the values of ΔE in amorphous cellulose or hemicellulose solutions: 230–545 kJ/mol). If we consider that the α process was only caused by molecular motions of sugars, it would be as almost impossible that the value of ΔE in wood was larger than the values of ΔE in amorphous cellulose or hemicellulose solution. That is to say, we must consider that the difference between values of ΔE might be related to the difference for situations of water molecules around sugars. Considering in the molecular order, water molecules with various situations (from abnormal water to bulk water) might exist in the sugar solution impregnated into the glass fiber filter paper. On the other hand, water molecules around sugars in wood with the water content under the fiber saturation point (FSP) might exist in confined rooms only. If we consider that the temperature location and the value of ΔE for the α process or the α' process are affected by situations of water molecules around sugars, it is satisfied that the α process differed from the α' process in some points. So, the α process in wood might be affected by the existing state or the sort of sugars.

Consequently, it could be clear that the thermal-softening behavior around −40°C was observed in not only the wood with the high moisture content but also the solutions of polysaccharides. Furthermore, it could be concerned that the thermal-softening behavior around −40°C in the wood with the high moisture content might be caused by water-swollen amorphous polysaccharides. However, to determine the nature of the mechanism for the relaxation process around −40°C, we must study further.

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