

Enthalpy relaxation behavior of dry wood detected by temperature-modulated differential scanning calorimetry

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Abstract Enthalpy relaxation of dry wood has been investigated by temperature-modulated differential scanning calorimetry. The reversing and non-reversing heat flow changes revealed that enthalpy relaxation occurred in dry wood, which did not exhibit any clear glass transitions. This enthalpy relaxation behavior seemed to differ significantly from those of previously reported isolated lignins, which implies that the microstructure of dry wood possesses a rigid amorphous state derived from interactions among wood components. The observed enthalpy relaxation is considered to be related to other components besides lignin, and the time-dependent physical properties due to unstable states or physical aging of wood originate not only from lignin but also from other components, such as cellulose and hemicellulose and the interactions between them.

Keywords Temperature-modulated differential scanning calorimetry · Enthalpy relaxation · Annealing · Physical aging · Drying

Introduction

Polymeric materials with glassy structures (glassy polymers) undergo enthalpy relaxation below their glass transition temperatures. Enthalpy relaxation is usually accompanied by a gradual reduction in volume (known as volume relaxation), which affects the physical properties of the material. The glass transition temperatures and enthalpy relaxation behaviors of industrial amorphous polymers (including composites) have been investigated by differential scanning calorimetry (DSC) with the aim of controlling their physical properties [1–7]. Some natural polymers such as food saccharides [8, 9], fibers [10–12] and wood derivatives [13–15] have been similarly investigated. Since the enthalpy relaxation time and the physical properties of a polymer are generally highly correlated, knowledge of the enthalpy relaxation of polymers can be used to estimate their usable lifetimes at ambient temperatures.

Wood is a natural polymer composite consisting of crystalline cellulose and amorphous matrices of cellulose, hemicellulose, and lignin. The wood matrix exhibits glass transitions. Since these glass transitions are affected by the presence of water in the matrix, the glass transition temperature of wood depends on the humidity and temperature of the environment. Many studies based on static and dynamic mechanical measurements have reported softening temperatures associated with a glass transition at about 80 °C for wet wood [16–22]. Some DSC and differential thermal analysis studies revealed the moisture dependence of the glass transition of wood and found that endothermic peaks are associated with the glass transition shift to lower temperatures with increasing moisture content (MC) of wood [23, 24]. Since it is difficult to detect such transitions in wood with an MC of less than 5 %, dry wood is not considered to have a clear glass transition. In a previous study [25] using

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temperature-modulated DSC, we found that the glass transition temperature of wood with a MC between 5 and 25 % could be detected as a step change in the reversing heat flow (RHF) and that exhibited a similar dependence on moisture as was reported in a conventional DSC studies; Besides, there is an endothermic peak in the non-reversing heat flow (NRHF) below the glass transition temperature. The endothermic peak in the NRHF may indicate enthalpy relaxation based on the apparent activation energy calculated from the Kissinger plot and the amount of enthalpy relaxation varies greatly with the MC of wood. Even in low moisture conditions, the thermal behavior of wood, especially variations in the NRHF, differs between the first and second heating runs. This suggests that wood with a low MC has a conformational disorder such as a rigid amorphous state [26, 27], which does not show pronounced glass transitions but generates enthalpy relaxation.

In this study, temperature-modulated DSC was used to investigate enthalpy relaxation of dry wood. The effects of the cooling rate and the holding time at a given temperature (which are referred to as the annealing time and temperature) on the thermal behavior [e.g., the temperature dependence of the total heat flow (THF)], which is equivalent to that measured by conventional DSC, as well as the dynamic heat capacity and NRHF are discussed. Based on the observed thermal behaviors, microstructure changes associated with unstable states of wood [28–30] are deduced.

Materials and methods

Sample preparation

An air-dried hinoki (*Chamaecyparis obtusa*) sample was cut into thin slices, which were up to 2 mm long in the longitudinal direction. From these slices, approximately $2 \times 2 \text{ mm}^2$ solid samples were cut. As a component of wood, ground cellulose fibers commercialized by Scientific Polymer Products, Inc. (LOT#05) were used.

For the DSC measurements, about 5 mg of these solid wood samples was placed in an aluminum pan with a pinhole; contact between the sample and the pan was maintained during heating/cooling runs and drying occurred through the pinhole. The same solid samples in pinhole hermetic pans were used in all the measurements for investigating the effects of the cooling rate and annealing. The same procedure was applied for the measurements of the cellulose sample.

DSC measurements

A heat flux differential scanning calorimeter (DSC Q100, TA Instruments) with modulation control was used. Modulated-

temperature DSC has been described by Reading and Schawe [31–34] and in our previous study [25].

In this study, three temperature programs were used to investigate the effects of the cooling rate and the temperature and annealing (holding) time at a given annealing temperature on the thermal behaviors of the samples between -80 and 170 °C, as shown in Fig. 1a–c. In all three programs, drying at 105 °C for 60 min by purging with dry nitrogen gas was performed prior to cyclic heating/cooling runs to ensure that the samples were completely dry. Program (a) was used to investigate the effect of the cooling rate. This program had 10 heating/cooling runs; the cooling rates of the fourth (3 °C/min), sixth (1 °C/min), and eighth runs (0.5 °C/min) differed from that (10 °C/min) of the other cooling runs, while the heating rate was fixed at 5 °C/min. Program (b) was used to investigate the effect of the cooling temperature. In this program, the minimum temperature T_{cl} before heating runs was increased in 20 °C intervals from -80 to 40 °C. The heating and cooling rates were set to 5 and 10 °C/min, respectively. Program (c) was used to investigate the effects of the holding time at annealing temperature T_a . It consisted of 15 heating/cooling cycles with isothermal runs at T_a (in the third, fifth, seventh, ninth, 11th, and 13th cycles) that had holding times of up to 240 min with alternating heating/cooling runs between -80 and 170 °C with heating/cooling rates of 5 °C/min. In this program, the heating histories immediately prior to annealing were designed to be the same. It should be careful about the generation of the thermal degradation of wood during DSC measurements, especially above 100 °C, when discussing the thermal behaviors in relation to the heating history. In the previous and preliminary studies [25], a weight loss derived from the thermal degradation resulted in less than 0.2 % in dry weight under the temperature range and heating/cooling rate conditions used in this experiment, and it was also confirmed that the thermal degradation rarely occurred in the conditions from the IR (Infrared) absorption at around 1745 cm^{-1} (C=O stretching) and 1245 cm^{-1} (C–O stretching).

Temperature-modulated DSC measures the RHF by modulating the temperature and the THF, which is equivalent to the heat flow obtained by conventional DSC. The RHF is obtained from the heat capacity change of a material, which responds rapidly to the oscillating temperature. The NRHF is defined as the difference between the THF and the RHF and it is originated from slow relaxation processes such as enthalpy relaxation. The temperature was modulated by applying a sinusoidal wave with a period of 100 s to the underlying heating/cooling programs. To maintain heating/cooling-only conditions for constant underlying cooling rates of 0.5 , 1 , 3 , 5 , and 10 °C/min, the amplitude was set to 0.13 , 0.26 , 0.79 , 1.32 , and

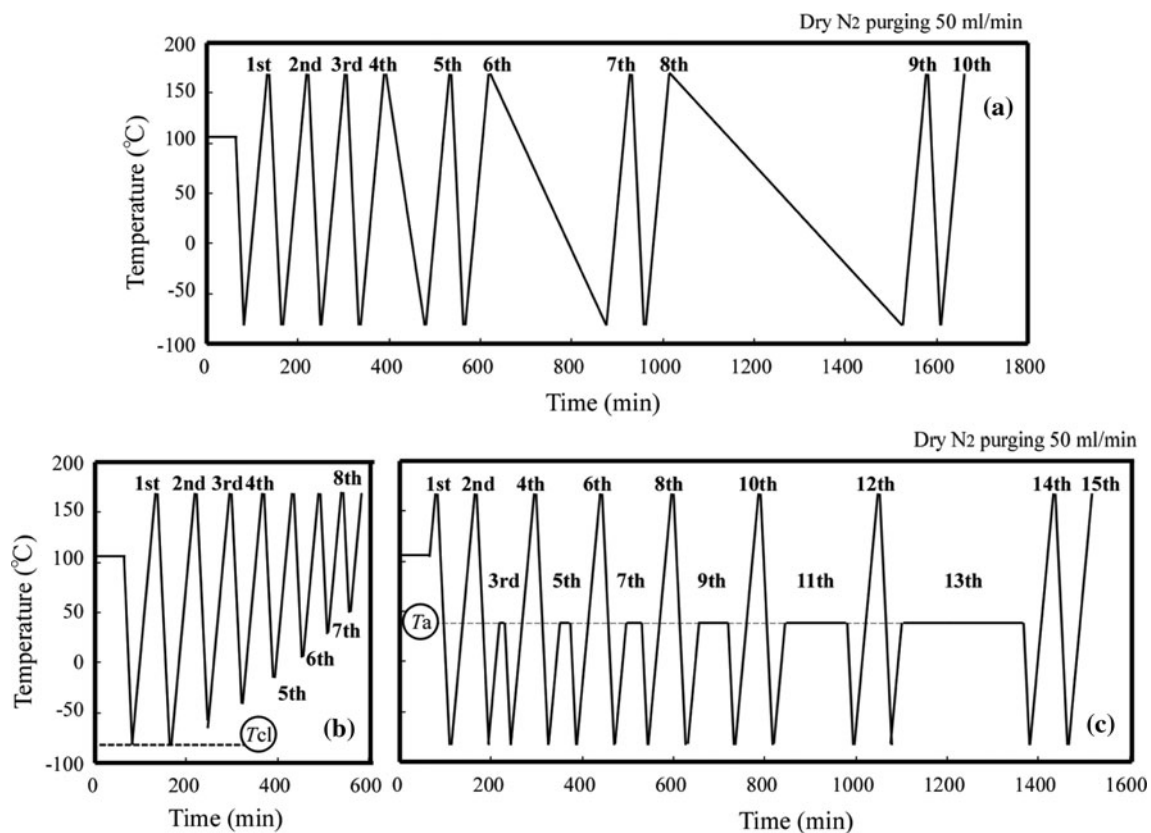


Fig. 1 Temperature programs of DSC used to investigate the effects of **a** cooling rate, **b** minimum cooling temperature, and **c** annealing temperature and holding time on the thermal behaviors of dry wood

2.65 °C, respectively, in program (a), whereas the amplitude was fixed to 1.0 °C in programs (b) and (c).¹ Empty pans with almost the same mass as the pans containing wood samples were used as reference samples.

When analyzing the results obtained by these programs, this study focuses on the heat flow during heating because different heat histories (e.g., different cooling rates and annealing conditions) drastically affect the thermal behavior during subsequent heating processes with the same heating rate.

Results and discussion

Total heat flow

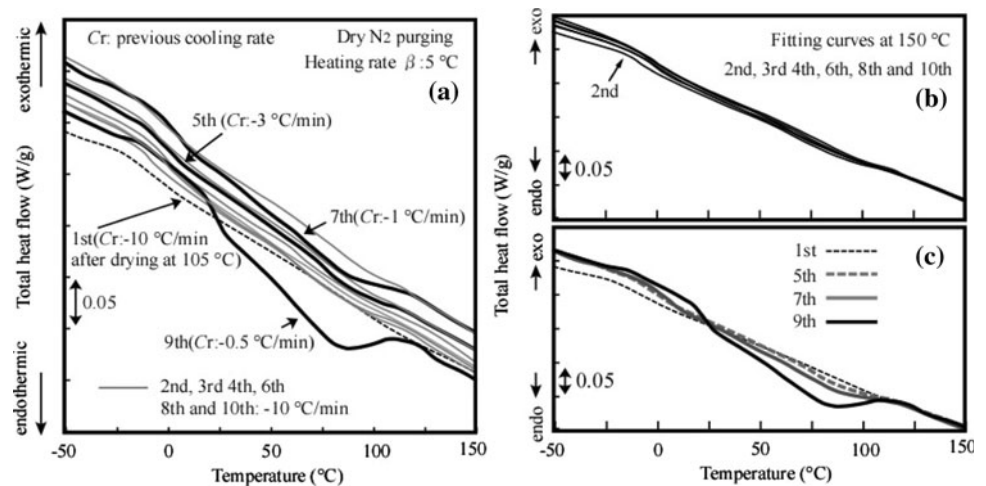
Figure 2a shows the THF behavior obtained when temperature program (a) was applied to dry solid hinoki. The thick lines in the figure indicate the THFs of the fifth, seventh, and ninth cycles, which have different heat histories and a cooling rate of 10 °C/min. The sample in the

first heating cycle (indicated by the dashed line) was previously dried at 105 °C for 60 min at which there is no heating history up to 170 °C. The previous cooling rate clearly affects the THF behavior in the following heating cycle; the faster cooling results in more exothermic behavior at a lower temperature and more endothermic behavior at higher temperatures. These behaviors are clearly apparent in Fig. 2b, c, which separates the THF shown in Fig. 2a into those with same and different heat histories, respectively. Heat flow curves are fitted at 150 °C by assuming that wood has similar heat flow behaviors at higher temperatures. As seen in Fig. 2b, samples that had previously been cooled at the same rate exhibit very similar heat flow behaviors, whereas samples that had been cooled at different rates have different heat flow behaviors (Fig. 2c). If the first run is used as a standard for comparison, exothermic behavior below about 25 °C and endothermic behavior between 25 and 100 °C are readily distinguishable.

Since the glass transition and enthalpy relaxation generate non-equilibrium states in glassy materials, it is important to consider the previous heat history (e.g., the cooling rate and time at the environmental temperature) before performing measurements on industrial polymers. Figure 2b suggests

¹ TA instruments, Choosing conditions in Modulated DSC, Thermal Analysis & Rheology Thermal application Note. TN-45B.

Fig. 2 **a** THF behaviors of wood with different cooling rates. THF curves for **b** same and **c** different prior cooling rates with curves superimposed over 150 °C



that dry wood samples that have been cooled at the same rate have no significant glass transition (manifested by a step change in the THF), although the slope of the THF changes slightly at about -20 °C. In addition to this change in the slope, the exothermic baseline is shifted in heating/cooling cycles. Dynamic mechanical analysis (DMA) of water-swollen wood revealed thermal softening at about -40 °C. This behavior is considered to originate from relaxation processes in water-swollen amorphous polysaccharides such as amorphous cellulose and hemicellulose [35]. Although DMA and DSC detect transitions by very different methods, the small change in the slope of the THF at about -20 °C might be a transition in the amorphous matrices in dry wood and sequential heating/cooling runs may stabilize the conformational structure in amorphous regions, as suggested by the shift in the exothermic baseline. The THF at about -20 °C in Fig. 2c gradually increases in exothermic energy with decreasing prior cooling rates in addition to a similar exothermic baseline shift. Reactions that release exothermic energy during heating include cold crystallization, adsorption, and curing. These reactions stabilize the fine structure to reduce the potential energy during heating. We conjecture that amorphous matrices in wood tend to aggregate or pack during heating after cooling to -80 °C.

Figure 3 shows the effect of the minimum cooling temperature on the THF behavior during heating measured by program (b); in this figure, the THF curves are fitted at 150 °C. The THF behavior clearly depends on the minimum cooling temperature prior to heating. The THF behavior of wood that had been cooled to -80 °C (indicated by the bold line) was similar to that shown in Fig. 2b. When the cooling minimum temperature was increased to -40 °C, the exothermic behavior at about -20 °C and the endothermic behavior at about 80 °C decreased, becoming too small to observe. For wood samples with minimum cooling temperatures of over -20 °C, the exothermic behavior (which was observed up to about 0 °C in Fig. 2b) disappeared and

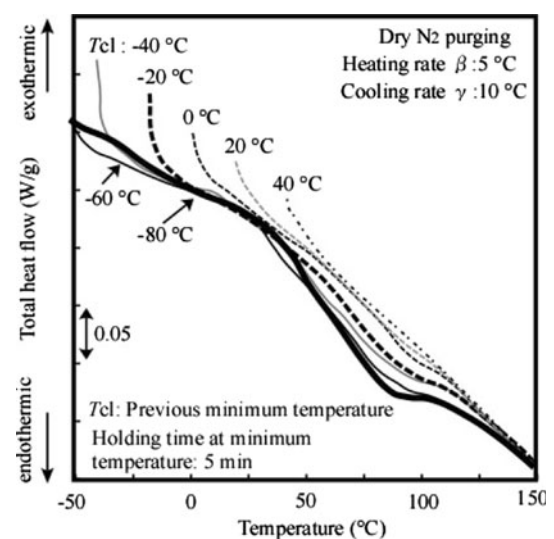


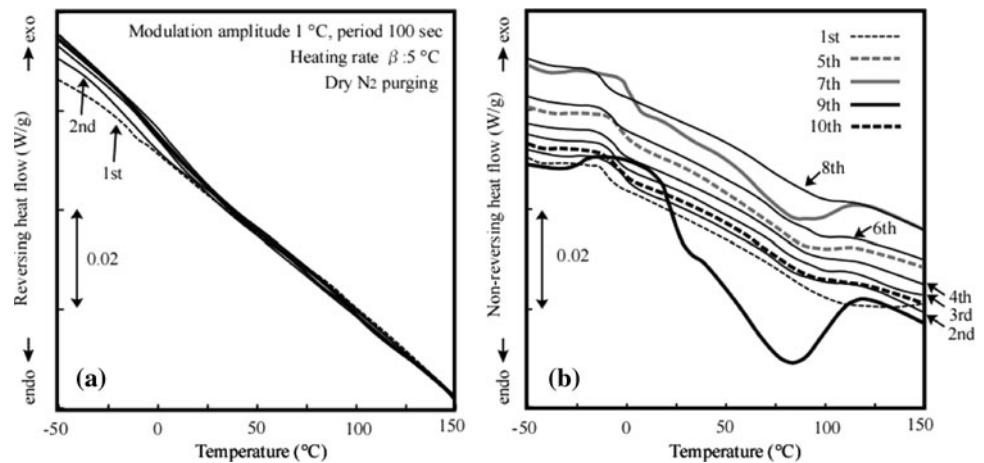
Fig. 3 Effect of minimum cooling temperature on THF behavior of wood during heating

further increasing the minimum cooling temperature caused less endothermic behavior. Distinct transitions in dry wood have not been reported by static and dynamic mechanical methods such as thermomechanical analysis and DMA. Cooling dry wood to temperatures lower than about -20 °C should reveal transitions during heating to high temperatures since there are expected to be transitions near -20 °C in dry wood. Other mechanical methods are needed to detect such transitions in dry wood and it is important to consider the effects of transitions that occur below 0 °C on the mechanical properties of dry wood.

Reversing heat flow and non-reversing heat flow derived by temperature modulation

Figure 4a, b, respectively, shows the RHF and NRHF behaviors of dry wood obtained by applying temperature

Fig. 4 RHF and NRHF behaviors of dry wood from temperature-modulated DSC data. **a** RHF: reversing heat flow, **b** NRHF: non-reversing heat flow



modulation while simultaneously measuring the THF (see Fig. 2a). The RHF (which is a component of the heat capacity) of the first and second heating runs at lower temperatures behaved differently from those of subsequent heating runs. Similar RHF curves were obtained after the third heating run over the measured temperature range. The THF results reveal that the heat capacity of dry wood is affected by the heat history and that the decrease in the dynamic heat capacity at $-20\text{ }^{\circ}\text{C}$ (calculated from the RHF) reached to $0.069\text{ J/g}^{\circ}\text{C}$ during the first and third runs. This reduced heat capacity at lower temperatures indicates a rigid structure in which molecular motion is restricted by cyclic heating and cooling runs. Except for the change in the RHF up to the third run at lower temperatures, the RHF differed very little above $0\text{ }^{\circ}\text{C}$ in subsequent runs, regardless of the prior cooling rate. This indicates that the heat history (including the cooling rate) does not greatly affect the dynamic heat capacity of dry wood at room temperature. In contrast, the NRHF (obtained by subtracting the RHF from the THF) showed pronounced changes at lower and higher temperatures. This NRHF behavior seems to be mostly determined by the THF behavior and both the exothermic and the endothermic behaviors of the THF originate from relaxation processes that mainly involve time-dependent phenomena. In addition to exothermic and endothermic behaviors, baseline shifts were also observed in the NRHF.

The glass transition and relaxation kinetics of glassy polymers have been characterized by conventional and temperature-modulated DSC [4–7]. By considering the holding temperature (i.e., the annealing temperature) and time, the enthalpy loss or enthalpy relaxation that accompanies glass transitions can be analyzed. However, unlike industrial polymers, dry wood does not show any clear glass transitions in its RHF behavior (see Fig. 4a). Nevertheless, enthalpy relaxation did occur in dry wood depending on the prior cooling rate (see Fig. 4b). It thus seems reasonable to conclude that dry wood contains both

disordered and relatively rigid microstructures such as a rigid amorphous state. It is not clear why baseline shifts were observed, but the observed variation in the endothermic/exothermic behaviors could be related to enthalpy relaxation.

Figure 5 shows the NRHF behavior of dry wood obtained by applying temperature program (c) to investigate the effect of the varying the annealing time at a constant annealing temperature of $0\text{ }^{\circ}\text{C}$. Measured NRHF curves are superimposed on the results above $150\text{ }^{\circ}\text{C}$ to discuss the enthalpy relaxation behavior. Discussion of the results focuses on temperatures above $0\text{ }^{\circ}\text{C}$ because little variation in the exothermic behavior is observed in Fig. 4 for temperature programs with the same minimum cooling temperature. The behavior becomes more endothermic with increasing annealing time. This implies that enthalpy relaxation occurs in dry wood, even though no pronounced transitions were detected. The enthalpy relaxation or physical aging of industrial polymers is almost always discussed in terms of their glass transitions because they are related to non-equilibrium thermodynamic states. Enthalpy relaxation of such polymers has often been observed at annealing temperatures up to $20\text{ }^{\circ}\text{C}$ below their glass transition temperatures. Even isolated lignins (lignin is a major component of wood), such as milled wood lignin and kraft lignin, exhibit enthalpy relaxation due to their glassy nature. Their enthalpy relaxation rates were highest at an annealing temperature of about $15\text{ }^{\circ}\text{C}$ below their glass transition temperatures (which are in the range $150\text{--}170\text{ }^{\circ}\text{C}$) [13]. Cellulose is another major component of wood. To the best of our knowledge, there has been no report of enthalpy relaxation in cellulose. The enthalpy relaxation behavior of the commercial cellulose observed in the annealing temperature at $0\text{ }^{\circ}\text{C}$ is shown, together with that of dry wood, in Fig. 5. It is found that the relaxation behavior of dry wood is similar to that of the cellulose. Cellulose is generally considered as a thermally stable and contains much crystalline portion. The cellulose

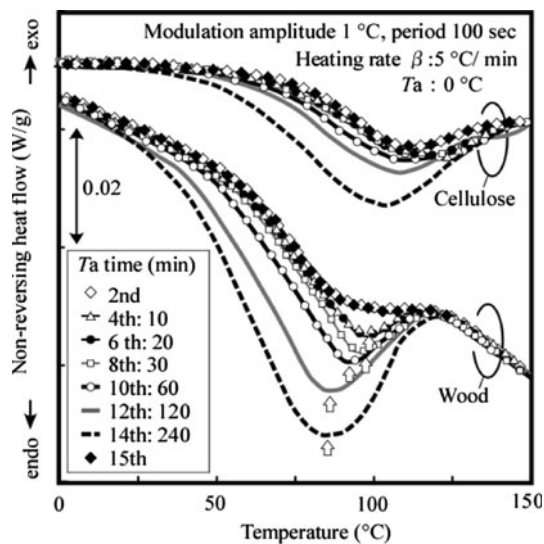


Fig. 5 Example of NRHF behavior of dry wood obtained by temperature program for examining the effect of the annealing time at a constant annealing temperature of 0 °C. The white arrows indicate the endothermic peak temperatures in the DSC heating runs after annealing

sample used in this study was subjected to powdering/grinding. By such processes the cellulose structure would change to more unstable or non-crystalline state, although there would be great differences in structure as well as thermal properties between native in situ cellulose and isolated celluloses. Since the relaxation process must occur in amorphous/non-crystalline portion, the observed relaxation behavior of the cellulose could be caused by the amorphous portion [35]. It is reported that cellulose powder with an MC of 5 % exhibited a glass transition at about 50 °C during cooling at a rate of 5 °C/min in DSC measurements [36]. Considering the moisture dependence, dry cellulose powder could have a glass transition above 50 °C. Furthermore, cellulose powder exhibits very weak, broad endothermic peaks associated with water loss around 25–140 °C in a cyclic heating/cooling up to 170 °C (the cellulose powder was considered to be dry in the second and third runs) [37]. There is another report concerned with the glass transition temperature of some food saccharides, such as xylose, glucose and maltose, and the glass transition temperatures of anhydrous those saccharides range in about 5–40 °C [8]. The observed relaxation might be derived from kinetics of hemicellulose with a similar structure of polymerized or conjugated xylose, glucose and maltose.

In the present DSC study of dry wood containing cellulose, hemicellulose and lignin, moisture adsorption/desorption (which is detected by weight gain/loss) was hardly observed during dry nitrogen purging in cyclic heating/cooling runs, even for annealing at 0 °C. Moreover, wood that has been dried for longer annealing times

exhibited greater endothermic behavior, even in later heating runs. Therefore, the endothermic behavior observed in the present study cannot be explained by water loss alone; it must also involve structural relaxation. Dry wood has a fine structure, which exhibits relaxation without typical glass transitions.

Enthalpy relaxation at various annealing temperatures

The enthalpy loss was determined from the area enclosed by heat flow curves after annealing at a given temperature and the base curve of the second heat flow. The effect of the annealing time at a given temperature on enthalpy relaxation was investigated (see Fig. 6). The enthalpy relaxation is greatly affected by the annealing temperature and the enthalpy loss was extremely high for annealing temperatures between –40 and 20 °C (especially at 0 °C). The enthalpy relaxation was very small at higher (80 °C) and lower (–60 °C) annealing temperatures. The enthalpy loss at $T_a = 20$ °C seemed to reach almost a constant for 720 min of the annealing time and this indicates that the observed relaxation process was all but completed by 720 min. By taking considerations to the effects of the annealing temperature and the time when the relaxation was completed, the relaxation equations would be discussed for dry wood.

At the annealing temperature of 0 °C, the enthalpy loss behavior of the cellulose was smaller than that of wood over the measured time due to much crystalline state. Based on the annealing temperature at which enthalpy relaxation occurs, the observed relaxation does not appear to mainly originate from lignin because isolated lignin has a glass transition temperature of over 150 °C [13–15].

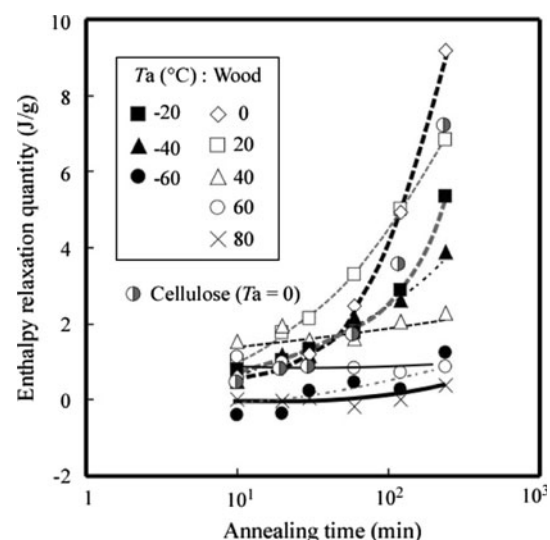


Fig. 6 Effect of annealing time at annealing temperatures on enthalpy relaxation of dry wood

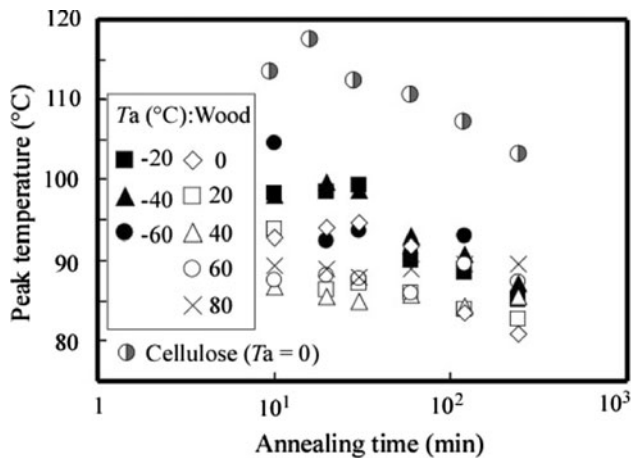


Fig. 7 Effect of annealing time on endothermic peak temperature determined from the NRHF of dry wood

Furthermore, more enthalpy relaxation was generated in a shorter time than in isolated lignins. Figure 7 shows the effect of the annealing time on the endothermic peak temperature (indicated by white arrows in Fig. 5). The peak temperature decreased with increasing annealing time for annealing temperatures below 20 °C, while it was almost constant for annealing temperatures above 20 °C. The peak temperatures of the cellulose appeared about 20 °C higher than those of wood annealed at 0 °C, indicating that the cellulose possesses a somewhat rigid structure involving both crystal and amorphous. The endothermic peak temperature generally increases as enthalpy relaxation proceeds in glassy materials (including lignin and cellulose) [13–15]. The shift in the peak temperature in Fig. 7 differs considerably from previous results for other polymers. This difference in the enthalpy relaxation behaviors and peak temperature shifts of dry wood and its isolated components may indicate differences in the fine structure and the molecular mobility. Although wood consists of three main components (cellulose, hemicellulose and lignin), the overall structure of these components with moisture exhibits quite complex physical, mechanical, rheological, and thermodynamic behaviors. In particular, the effects of amorphous components on these behaviors are currently unclear. The compatibility between amorphous and crystalline cellulose will affect these behaviors. Most mechanical studies of moist wood conclude that the softening behavior derived from the glass transition depend on the properties of lignin. In this study, the enthalpy relaxation behaviors of dry wood were measured by DSC and transitions due to other components besides lignin were detected. Investigation of the difference between wood properties and those of isolated components may provide a new model of wood microstructure that accounts for the time-dependent physical properties on

temperature and moisture dependence in terms of unstable states of wood.

Conclusion

Temperature-modulated DSC clearly detected enthalpy relaxation of dry wood from the NRHF, although no clear glass transitions were observed in the RHF. The enthalpy relaxation is greatly affected by the annealing temperature and holding time. It was maximized at an annealing temperature of about 0 °C. Very little enthalpy relaxation was observed at temperatures above 40 °C or below –60 °C for holding times of up to 250 min. The endothermic peak temperature in the relaxation decreased when the annealing time was increased. These results suggest that temperature changes alter the microstructure of wood (even dry wood) and that lignin exists in different structures in wood because their enthalpy relaxation behaviors are quite different from those of isolated lignin. In particular, the observed enthalpy relaxation could be related to the other components besides lignin so that the time-dependent physical properties due to unstable states of wood originate from not only lignin but also from other components such as cellulose and hemicellulose and their interactions.

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