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Influence of heating and drying history on micropores in dry wood

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Abstract To investigate the influence of heating and drying history on the microstructure of dry wood, in addition to the dynamic viscoelastic properties, CO₂ adsorption onto dry wood at ice–water temperature (273 K) was measured, and the micropore size distribution was obtained using the Horvath-Kawazoe (HK) method. Micropores smaller than 0.6 nm exist in the microstructures of dry wood, and they decreased with elevating out-gassing temperature and increased again after rewetting and drying. Dry wood subjected to higher temperatures showed larger dynamic elastic modulus (E') and smaller loss modulus (E''). This is interpreted as the result of the modification at higher temperature of the instability caused by drying. Drying history influenced the number of micropores smaller than 0.6 nm in dry wood not subjected to high temperature, although the difference in the number of micropores resulting from the drying history decreased with increasing out-gassing temperature. A larger number of micropores smaller than 0.6 nm exist in the microstructure of dry wood in more unstable states, corresponding to smaller E' and larger E'' than in the stable state. Consequently, unstable states are considered to result from the existence of temporary micropores in the microstructures of dry wood, probably in lignin.

Key words Dry wood · Unstable state · Dynamic viscoelastic property · Micropore structure · HK method

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Introduction

A new concept for the physical properties of wood was recently reported.^{1–7} Wood subjected to changes in temperature and/or swelling state shows a lower elastic modulus and greater fluidity judging from creep or stress relaxation measurements than wood kept for a long time under constant temperature and humidity. This is interpreted as a result of the instability caused by localized stress in the microstructures of wood cell walls caused by changes in environmental conditions such as temperature and humidity. These stresses weaken intermolecular and intramolecular hydrogen bonds and lower resistance to deformation. In addition to those reports, Nakano⁸ interpreted that the increase in relaxation caused by quenching was due to the free volume temporarily created by freezing the molecular chain motion of wood components, most probably lignin, during quenching, although the amount of free volume was not measured directly. A similar phenomenon, called physical aging, is well known for various amorphous polymers and is explained by the free volume concept.^{9,10}

In our previous report,¹¹ we attempted to clarify the influence of heating history on the dynamic viscoelastic properties and dimensions of dry wood. Unstable states of dry wood still existed after heating at 105°C for 30 min and were modified by activated molecular motion in the first heating process to higher temperatures above 105°C. However, information about free volume from the results of dimensional change was difficult to obtain because wood has anisotropy of dimensional change and is porous.

To understand the physical and mechanical properties of unstable wood, measuring extremely fine structures of wood is thought to be very effective. Therefore, in the present study, in addition to measuring the dynamic viscoelastic properties, to get more information about the microstructures of dry wood with various heating and drying histories, adsorption of CO₂ was measured at ice–water temperature (273 K). The micropore size distribution was obtained using the Horvath-Kawazoe (HK) method,¹² which is suitable for measuring micropore structures smaller than 2 nm.

Materials and methods

Materials

Test samples were taken from the outer region of a log of Japanese hinoki (*Chamaecyparis obtusa* Endl.). The size to measure dynamic viscoelastic properties was 30 mm radial (R), 3 mm tangential (T), and 1 mm longitudinal (L). To measure CO₂ adsorption for the determination of pore-size distribution, the samples were cut into small cubes with sides generally smaller than 2 mm. Samples were boiled for 1 h and annealed at room temperature, then dried and conditioned in a room [20°C and 65% relative humidity (RH)] for more than 1 month. The detailed heating and drying conditions prior to the dynamic viscoelastic and adsorption measurements are presented below.

Methods

Measurement of dynamic viscoelastic properties

The temperature dependence of the dynamic elastic modulus (E') and loss modulus (E'') was measured by the tensile forced-oscillation method using an automatic dynamic viscoelastometer (Seiko Instruments, DMS6100). Measurements were conducted in dry air over a temperature range of about 20°–180°C for dry wood at a programmed heating and cooling rate of 3°C/min. Frequencies of the measurement were 0.5, 1, 2, 5, and 10 Hz, the span was 20 mm, and the displacement amplitude was 5 μ m. The tensile direction was radial.

Measurement of micropore structure

For analysis of the micropore structure, about 1 g of the sample was put into a sample cell for adsorption measurement of CO₂. The cell was out-gassed for 5 h or more under a high vacuum (<10⁻⁵ Pa) at a predetermined temperature from 30° to 190°C. The CO₂ amount adsorbed was measured at ice–water temperature (273 K) with 5 min of adsorption time, which was reported as the most appropriate condition to test wood micropores,¹³ using an automatic gas adsorption device, AUTOSORB-1 (Quantachrome, USA). The pore-size distribution of micropores below 0.6 nm was determined using the HK method from the adsorption isotherms obtained.

Results and discussion

Influence of heating history on dynamic viscoelastic properties of dry wood for temperatures from 20° to 180°C

Samples in air-dry condition were dried by out-gassing at around 25°C for 1 day, and then set in the analyzer. Figure 1 presents the measuring program for the results shown in Fig. 2. Figure 2 shows the influences of heating history on

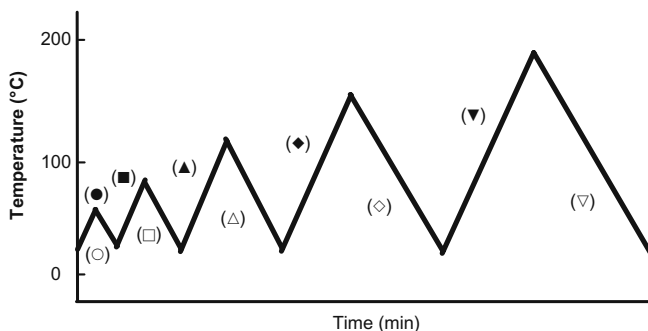


Fig. 1. Temperature program for measurement of dynamic viscoelastic properties from 20° to 180°C shown in Fig. 2. Symbols correspond to those used in Fig. 2

dynamic viscoelastic properties at 0.5 Hz in the radial direction of dry wood in heating and cooling processes at a programmed heating and cooling rate of 3°C/min. Only dynamic viscoelastic properties measured at 0.5 Hz are shown, because the most typical tendency was recognized at 0.5 Hz and similar tendencies were obtained at other frequencies. Relative E' , which is relative to the first heating at 30°C, was smaller in each heating process than in the corresponding cooling process. Relative E'' , which is relative to the first heating at 30°C, and $\tan \delta$ were larger in each heating process than those values for the corresponding cooling process. Behavior in the heating process was almost the same as just before the cooling process in the same temperature ranges. On the other hand, above the temperature range experienced, lower relative E' , and higher relative E'' and $\tan \delta$ are shown in the heating process than in the corresponding cooling process. These results indicate that the microstructures of dry wood components become stabilized with rising temperature, and that instability in the microstructure of dry wood by cooling, if it occurs, is far less than that caused by drying.

A similar tendency has been observed in the temperature range from 100° to 200°C.¹¹ The cause of these results has been considered as follows. When wet wood is dried, localized stresses occur in the microstructures of wood components in cell walls. Those stresses weaken intermolecular and intramolecular hydrogen bonds and lower resistance to deformation. The above result suggests that wood microstructures in a more unstable state of dry wood have looser structure, and unstable microstructures of dry wood stabilize with increasing temperature, thus having a tighter structure subjected to higher temperature.

Micropore structure of wood

Wood is a porous material, and the pores can be divided into two categories: macropores ranging from 0.1 μ m to a few hundred micrometers, and micropores smaller than 10⁻⁸ m in the cell wall. Sawabe et al.¹⁴ examined the pore structure in the cell wall by nitrogen adsorption at liquid nitrogen temperature (77 K); however, they encountered a technical problem associated with the method of analyzing

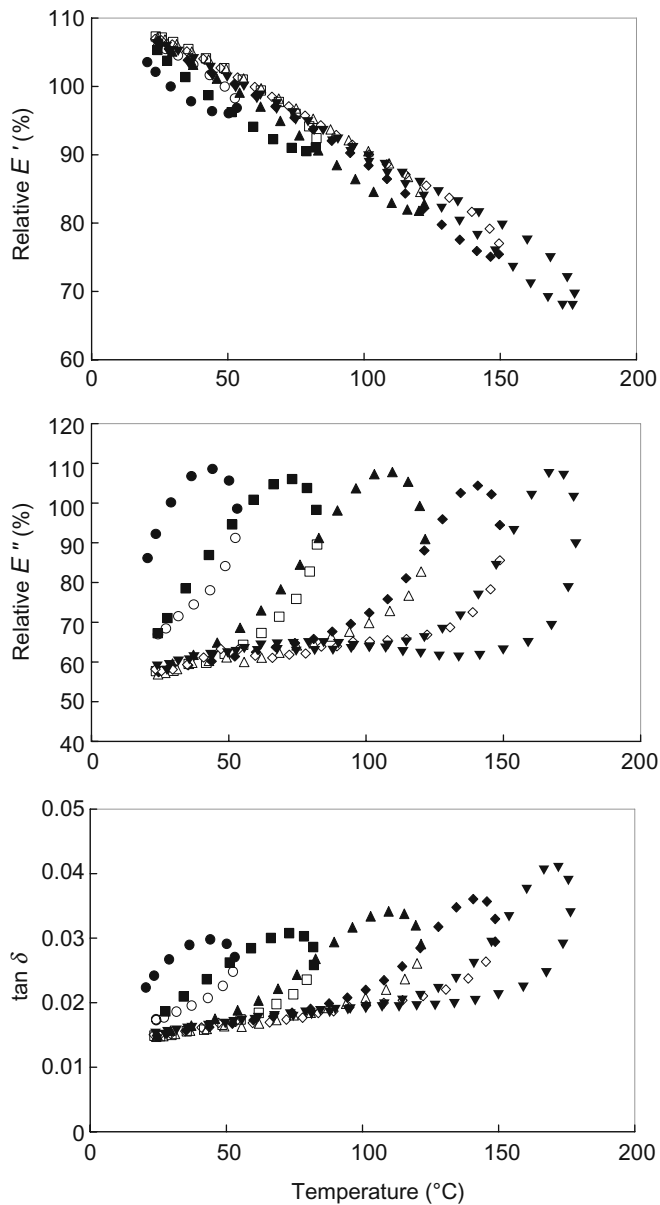


Fig. 2. Influences of heating on dynamic viscoelastic property of dry wood at 0.5 Hz in the radial direction of dry wood. Relative E' and relative E'' are relative to values at 30°C in the first heating process. Circles, between 20° and 50°C; squares, between 20° and 80°C; triangles, between 20° and 120°C; diamonds, between 20° and 150°C; inverted triangles, between 20° and 180°C; filled symbols, heating processes; open symbols, cooling processes

the pore structure to obtain detailed findings concerning the micropore structure on the subnanometer scale. Thus, the micropore structure was not examined. In recent years, the micropore structure of wood and bamboo charcoals and wood have been successfully measured at ice–water temperature (273 K) with CO_2 by Akitomo et al.¹⁵ and Nakatani et al.¹³ When considering the relation to the unstable state in the microstructure of dry wood, investigating the micropore structure is very important. Therefore, in this study, micropores in dry wood were measured with a method similar to that used in those reports.^{13,15}

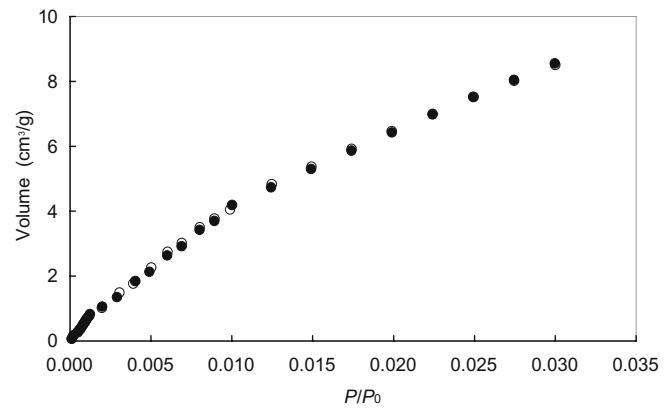


Fig. 3. Adsorption isotherms of CO_2 onto wood. Different symbols indicate results of different samples pretreated similarly before measurement

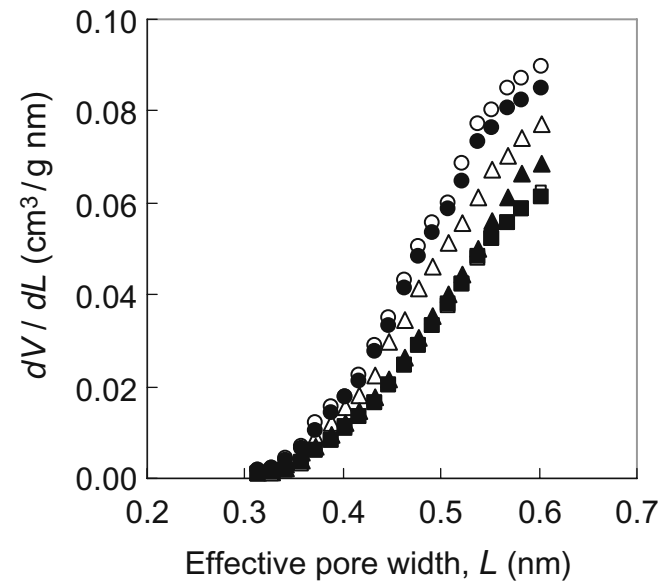


Fig. 4. Pore-size distributions determined by the adsorption of CO_2 with samples dried by out-gassing at different temperatures. Open circles, out-gassed at 30°C; filled circles, at 50°C; open triangles, at 80°C; filled triangles, at 130°C; open squares, at 160°C; filled squares, at 190°C

Reproducibility of the gas adsorption method for dry wood

Figure 3 shows adsorption isotherms for adsorption of CO_2 onto different samples at ice–water temperature (273 K) and below 0.03 of relative pressure, which is the upper limit in this measurement condition for the apparatus used. The results demonstrated high reproducibility for the method when the sample was conditioned in the same manner.

Influence of heating history on micropore size distributions of dry wood

Figure 4 shows the influence of the out-gassing temperature on micropore size distributions smaller than 0.6 nm. Samples conditioned at 20°C and 65% RH were dried by out-gassing

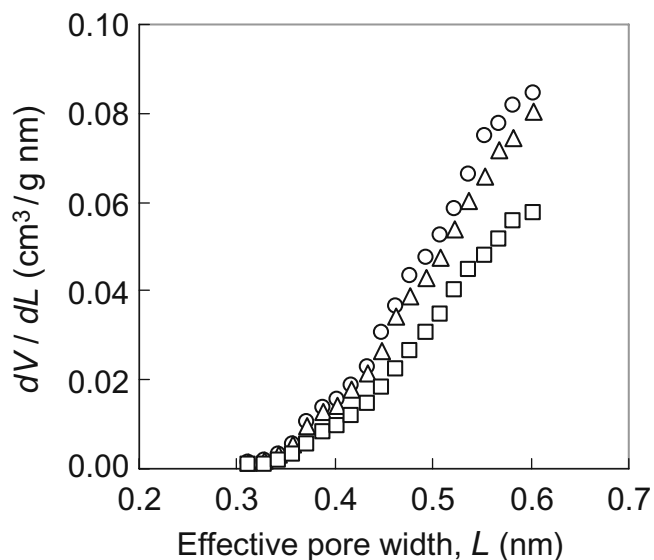


Fig. 5. Pore-size distributions determined by the adsorption of CO_2 with the same sample repeatedly out-gassed at different temperatures. *Open circles*, first measurement after out-gassing at 30°C ; *open triangles*, second measurement after out-gassing at 50°C ; *open squares*, third measurement after out-gassing at 170°C

at 30°C for 1 day, and at 50° , 80° , 130° , 160° , or 190°C for 5 h before adsorption measurements. Pore volume within this range decreased with increases in out-gassing temperature. This means that microstructures of dry wood were tighter at higher temperature. Therefore, this result can explain the result of dynamic viscoelastic properties shown in Fig. 2.

Figure 5 shows the influence of heating history on micropore size distributions for pores smaller than 0.6 nm. Samples were conditioned at 20°C in a desiccator containing dry silica gel and CaCl_2 for more than 1 month; they were then dried by out-gassing at 30°C for 1 day and analyzed, then dried by out-gassing at 50°C for 5 h and analyzed, and then dried by out-gassing at 170°C for 5 h and analyzed. The result in Fig. 5 shows that the number of micropores smaller than 0.6 nm decreased with higher out-gassing temperature. In relation to these results, Stone and Scallan¹⁶ reported that several wood pulps, cellulose, xylan, and lignin were dried by a solvent-exchange procedure and their specific surface areas were measured by nitrogen adsorption, showing that a substantial drop in surface area occurred by heating in dry nitrogen, although the micropore structure was not measured.

When wood is dried, localized stresses are produced in the microstructure of wood components in cell walls. According to Goring,¹⁷ the softening temperatures of dry wood components are 134° – 235°C for lignin, 165° – 217°C for hemicelluloses, and 231° – 253°C for cellulose. An unstable state in the microstructures of dry wood is considered to exist at temperatures from 30° to 190°C , because dry wood components do not entirely surpass glass transition temperatures in this temperature range,^{17,18} as mentioned in the previous report.¹¹ Thus, they have not completely approached the stable state at these temperatures.

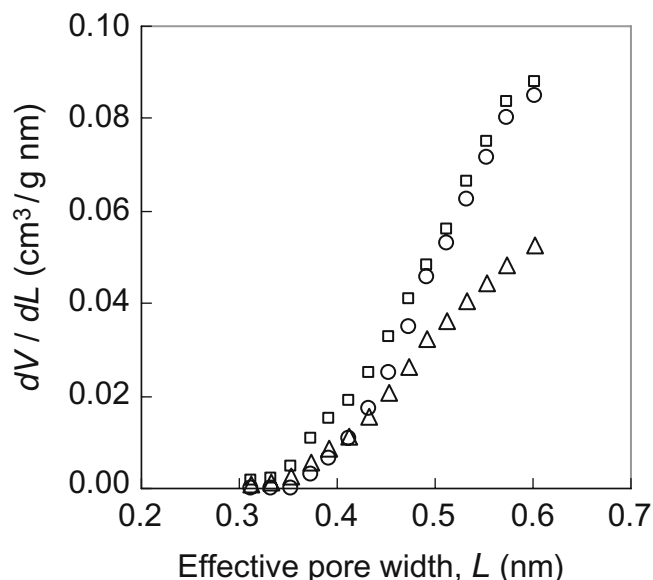


Fig. 6. Influence of rewetting and drying on pore-size distributions determined by the adsorption of CO_2 with the same sample. *Open circles*, dried by out-gassing at 50°C ; *open triangles*, second measurement after out-gassing at 110°C ; *open squares*, third measurement after boiling and drying at 20°C and 65% relative humidity (RH) for several days and out-gassing at 50°C

As stated above, more micropores are considered to be produced in more unstable states because of localized stress in the microstructures of dry wood. If this deduction is correct, it is expected that micropores once decreased by heating should increase again after rewetting followed by drying.

Figure 6 shows the micropore size distribution of the sample after drying by out-gassing at 50°C for 5 h, then by out-gassing at 110°C for 5 h, then boiled and dried at 20°C and 65% RH for several days, followed by out-gassing at 50°C for 5 h. The behavior of the micropore size distribution after boiling and drying was similar to that in the first measurement, and, interestingly, the smaller micropores seemed to increase. This means that a more unstable state occurred in the microstructure of dry wood immediately after boiling and drying than in wood dried after conditioning at 20°C and 65% RH for several days.

Influence of drying history on micropore size distributions of dry wood

To investigate the influence of drying history on micropore size distributions of dry wood, samples with different drying histories are compared in Fig. 7. Samples were conditioned at 20°C in a desiccator containing dry silica gel and CaCl_2 or conditioned at 20°C and 65% RH for more than 1 month, then dried by out-gassing at 30°C for approximately 1 day or 50°C for 5 h and then analyzed. Figure 7 shows that differences in the drying history affected micropore size distributions when dried by out-gassing at 30°C , and the number of micropores in the sample conditioned in a desiccator

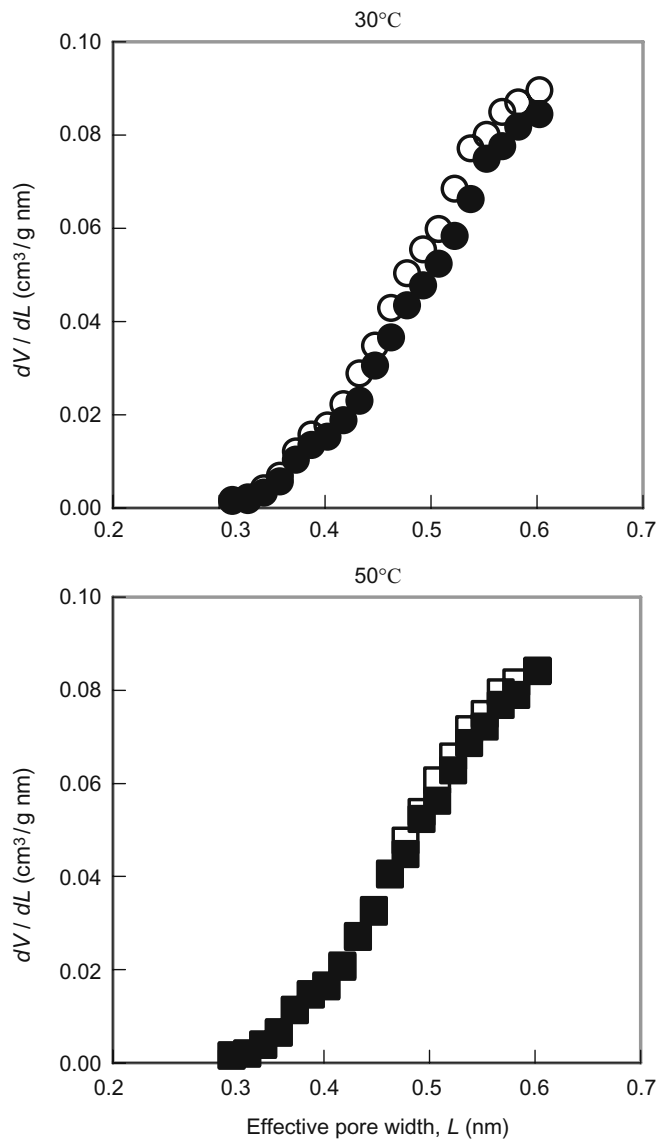


Fig. 7. Influence of drying history on pore-size distributions determined by the adsorption of CO_2 with different conditioned samples. *Open symbols*, conditioned at 20°C and 65% RH; *filled symbols*, conditioned at 20°C and 0% RH. *Circles*, out-gassed at 30°C ; *squares*, at 50°C

cator containing dry silica gel and CaCl_2 was clearly smaller than that for the sample conditioned at 20°C and 65% RH before drying. This means that the former sample was more stable than the latter, because the former was kept for a longer time in a dried state than the latter. However, comparing the samples dried by out-gassing at 50°C , the difference was hardly noticeable. From this result, it became clear that drying history influenced micropores smaller than 0.6 nm at relatively low temperature and more micropores existed in the more unstable states, although differences in the number of micropores decreased when subjected to a higher temperature. A similar tendency was reported concerning the mechanical properties of wood dried at different rates and temperatures.¹⁹

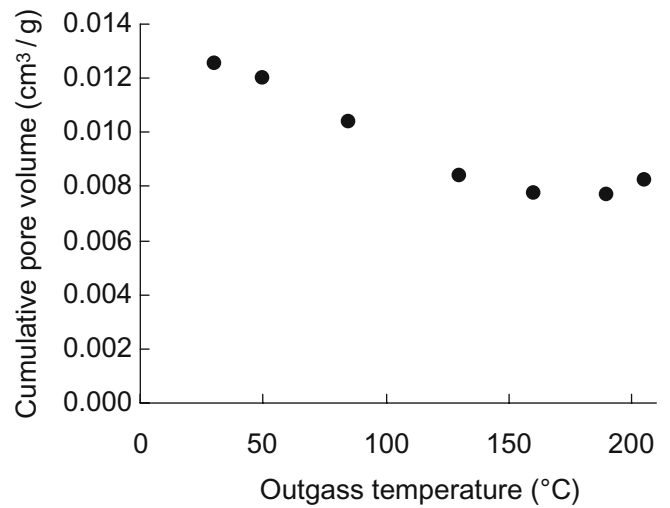


Fig. 8. Dependence of cumulative pore volume of micropores smaller than 0.6 nm on out-gassing temperature (from results shown in Fig. 4)

Dependence of cumulative pore volume of micropore on out-gassing temperature

Figure 8 shows the dependence of cumulative pore volume of micropores smaller than 0.6 nm, which was obtained from the result shown in Fig. 4, on out-gassing temperature. In changing the out-gassing temperature from 30° to 160°C , the cumulative pore volume decreased almost linearly; however, it increased slightly with out-gassing temperature when above 160°C , probably resulting from the degradation of wood components. The cumulative pore volume decreased by approximately 40% when heating from 30° to 160°C .

Nakatani et al.^{13,20} confirmed that most micropores smaller than 0.6 nm in wood existed in lignin, as determined by the adsorption of various organic liquids and the adsorption of CO_2 . Considering this report and the result of Fig. 8, temporary micropores smaller than 0.6 nm related to the unstable microstructures of dry wood probably exist in lignin. To confirm this, further investigation is needed in the near future.

From the results above, it is clear that dry wood in unstable states (smaller relative E' , and larger relative E'' and $\tan \delta$ than in the stable state) has more micropores smaller than 0.6 nm; moreover, unstable dry wood stabilizes with elevating temperature. The unstable state of wood caused by drying is considered to be attributable to the existence of temporary micropores in the microstructures.

Conclusions

To investigate the influence of heating and drying history on micropores in dry wood, dynamic viscoelastic properties and CO_2 adsorption at ice–water temperature (273 K) were measured. The results obtained are as follows. Temporary micropores smaller than 0.6 nm exist in the microstructure

of dry wood, and they decrease in number with an increase in out-gassing temperature and are also affected by the drying history. More micropores smaller than 0.6 nm exist in the microstructure of dry wood in the more unstable states with smaller relative E' and larger E'' and $\tan \delta$. The unstable state caused by drying is considered to result from the existence of temporary micropores in the microstructures of dry wood, probably in lignin.

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