

ORIGINAL ARTICLE

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Micropores and mesopores in the cell wall of dry wood

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Abstract To investigate micropores and mesopores in the cell walls of dry wood, CO₂ gas and N₂ gas adsorption onto dry wood were measured at ice-water temperature (273 K) and liquid nitrogen temperature (77 K). CO₂ gas adsorption isotherms obtained were used for determining micropore volumes smaller than 0.6 nm by the HK method (Horvath-Kawazoe method), and N₂ gas adsorption isotherms obtained were used for determining the mesopore volume between 2 nm and 50 nm by the Barrett-Joyner-Halenda (BJH) method. Micropores and mesopores existed in cell walls of dry wood, and the cumulative pore volume was much larger for micropores than for mesopores. Micropores in the cell wall of dry wood decreased with elevating heat treatment temperature, and the decreased micropore was reproducible by wetting and drying. Mesopores did not decrease so much with elevating heat treatment temperature. Micropore volumes for the softwood Hinoki and the hardwood Buna were compared. A larger amount of micropores existed in hardwood Buna than in softwood Hinoki, and this relationship was considered to correspond to the difference in thermal softening properties for lignin in water-swollen Hinoki and Buna. This result probably indicates that micropores in the cell walls of dry wood relate to the structure of lignin.

Key words Dry wood · Micropore · Mesopore · N₂ gas adsorption · CO₂ gas adsorption

Introduction

Wood is a porous material, and it has pore structures in the cell wall. Studies¹ about the pore structure of wood have been conducted for many years for the basis of producing wood pulp and understanding the physical properties such as specific gravity and moisture content, the transfer of matter, and the physical and chemical reaction site. Sawabe et al.^{2,3} studied widely the pore structures in the cell wall of wood and the pore structure of wood constituents by N₂ gas adsorption at liquid nitrogen temperature (77 K). Pore-size distribution, surface area, and pore volume were reported for swollen wood, dry wood, cellulose, and lignin. Stone et al.^{4,5} also investigated the pore structure of wood by N₂ gas adsorption and reported the effect of component removal on the porous structure of the cell wall of wood. In those reports, however, only the mesopores of wood were discussed, and the micropores were not directly measured.

Pores in the cell wall of dry wood can be divided into two categories: mesopores, ranging from 2.0 to 50 nm, and micropores, smaller than 2.0 nm. Sawabe et al.^{2,3} have reported a series of studies about the pore structure in the cell wall by N₂ gas adsorption at liquid nitrogen temperature (77 K). However, they encountered a technical problem associated with the method of analyzing the micropore structures. Therefore, the micropores in the cell wall of dry wood have not been sufficiently investigated. In recent years, success in measuring the micropores of bamboo charcoal and wood, using CO₂ gas adsorptions at ice-water temperature (273 K), has been reported by Akitomo et al.,⁶ Nakatani et al.,⁷ and Kojiro et al.^{8,9} It has recently become possible to measure the micropores. When considering the pore structure in cell walls of dry wood, micropores should be investigated as well as mesopores.

In previous reports,^{8,9} we have attempted to clarify the influence of heating history on the microstructures of dry wood. Adsorbed amounts of CO₂ gas were measured at ice-water temperature (273 K), and micropore size distributions were determined using the HK method,¹⁰ which is suitable for measuring micropore structures below 2 nm. It

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was revealed that the cumulative volume of micropores smaller than 0.6 nm in dry wood decreased with increasing heating temperature or with elapsed time of environment. In addition to those results concerning micropores, it was indicated that the changes in micropore volume were related to the mechanical properties of wood in unstable state, meaning the transition process to the thermodynamic equilibrium state.^{11–13} Further information about micropores is needed for understanding the relationship between mechanical properties and microstructures of wood.

Therefore, in this report, to clarify the entire picture of pore structures in cell walls of dry wood, the effects of heating history on pore volumes for micropores and mesopores as well as the difference in pore volumes between softwood and hardwood were investigated. Measurements used for the discussion were adsorption of CO₂ gas at ice-water temperature (273 K) and of N₂ gas at liquid nitrogen temperature (77 K), and dynamic viscoelastic properties.

Materials and methods

Materials

Test samples were taken from the outer region of a log of Hinoki (*Chamaecyparis obtusa* Endl.) and one of Buna (*Fagus crenata* Bl.). The sample size for measuring dynamic viscoelastic properties was 30 mm radial (R), 3 mm tangential (T), and 1 mm longitudinal direction (L); for measuring CO₂ and N₂ gas adsorption, wood samples were cut into small cubes with edge length around 2 mm or smaller. Samples were boiled for 1 h and cooled slowly to room temperature, and then they were dried and conditioned in a room (20°C and 65% RH) for more than 1 month. The detailed heating and drying conditions before the dynamic viscoelastic properties and gas adsorption measurements are presented later.

Methods

Measurement of gas adsorption

About 1.5 g of the sample for CO₂ gas adsorption analyzing the micropores and about 4.5 g of sample for N₂ gas adsorption analyzing the mesopores, respectively, were put into sample cells and out-gassed for 5 h or more at 50°C under a high vacuum below 10⁻⁵ Pa. For heat treatments, samples were out-gassed for 1 h at predetermined temperatures from 50° to 160°C after out-gassing for 5 h or more at 50°C. The adsorbed amounts of CO₂ gas and N₂ gas were measured at ice-water temperature (273 K) and at liquid nitrogen temperature (77 K), respectively, with 5 min of adsorption time, using an automatic gas adsorption device, AUTOSORB-1 (Quantachrome, USA). Examples of adsorption isotherms are shown below. From the adsorption isotherms of N₂ gas, micropore volume below 0.6 nm was determined by using the HK method,¹⁰ which is suitable

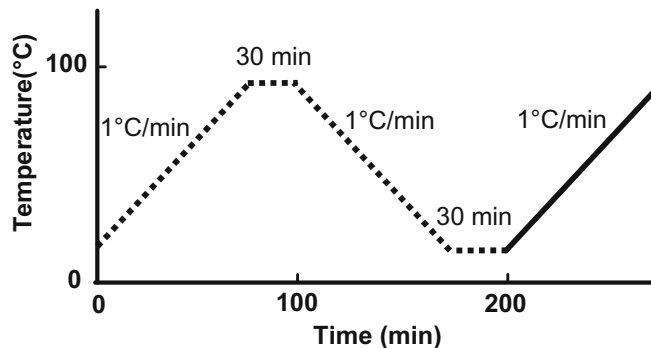


Fig. 1. Temperature program for measurements of dynamic viscoelastic properties from 20°C to 95°C shown in Fig. 7. *Solid line* corresponds to the temperature program used in Fig. 7; *dashed line* corresponds to the pretreatment process

for micropore analysis and is assumed for the slit-like pores. From the adsorption of CO₂ gas, mesopore volume between 2 nm and 50 nm was determined by the BJH method,¹⁴ which is suitable for mesopore analysis and is assumed for the cylindrical pores.

Measurement of dynamic viscoelastic properties

The temperature dependences of the dynamic elastic modulus (E') and $\tan\delta$ were measured by the tensile forced-oscillation method using a thermal mechanical analyzer (Seiko Instruments; TMA/SS6100). Measurements were conducted in water over a temperature range from 20° to 95°C for water-swollen wood at a programmed heating and cooling rate of 1°C/min. Frequency of the measurement was 0.05 Hz, the span was 20 mm, and the load amplitude was 0.49 N \pm 0.29 N. The tensile direction was radial. To minimize the effect of cooling history on dynamic viscoelastic properties, samples were conditioned for having the same histories. Figure 1 shows the temperature program for measurements of dynamic viscoelastic properties from 20° to 95°C shown in Fig. 7.

Results and discussion

Effect of pretreatment on micropore and mesopore volumes of dry wood

Figure 2 shows the adsorption isotherm of CO₂ gas at ice-water temperature (273 K) onto wood dried by out-gassing at 50°C for 5 h. The measuring relative pressure ranges were below 0.03. Figure 3 shows the adsorption isotherm of N₂ gas at liquid nitrogen temperature (77 K) onto wood dried by out-gassing at 50°C for 8 h. The measuring relative pressure ranges were from 0.2 to 0.95. Examples of cumulative pore volumes for micropores and mesopores of dry wood are shown in Figs. 4 and 5. Pore volumes were determined, respectively, by applying the HK method,¹⁰ which is suitable for micropore analysis, to the results of Fig. 2 and by applying the BJH method,¹⁴ which is suitable for

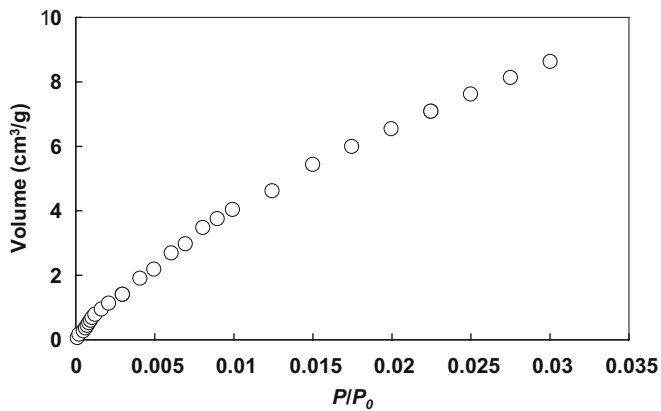


Fig. 2. Adsorption isotherm of CO₂ gas at ice-water temperature (273 K) onto Hinoki dried by out-gassing at 50°C

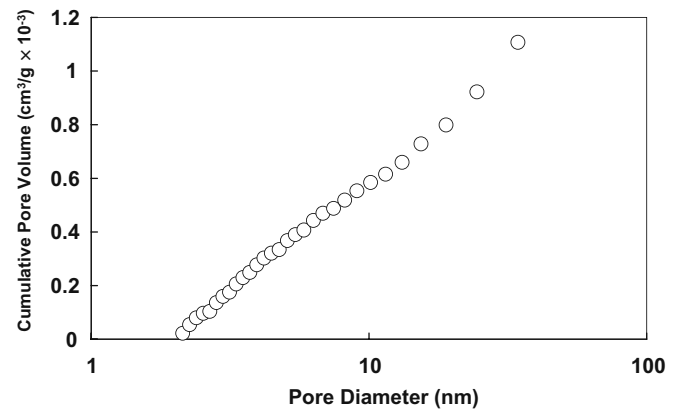


Fig. 5. Cumulative pore volume determined by the results of Fig. 3

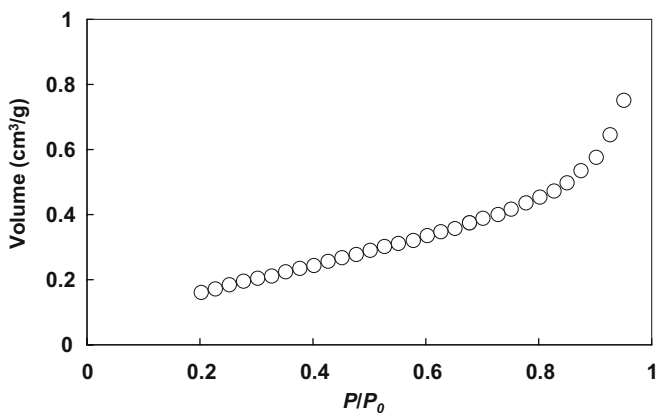


Fig. 3. Adsorption isotherm of N₂ gas at liquid nitrogen temperature (77 K) onto Hinoki dried by out-gassing at 50°C

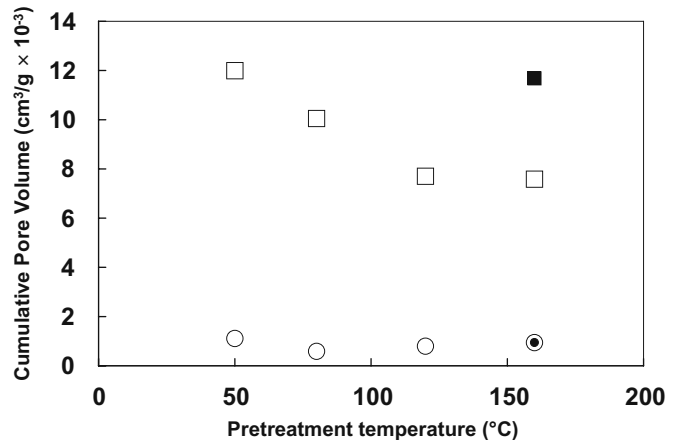


Fig. 6. Effect of pretreatment on cumulative pore volume of micropores and mesopores determined by the adsorptions onto dry Hinoki of CO₂ gas at ice-water temperature (273 K) and of N₂ gas at liquid nitrogen temperature (77 K). *Open circles*, mesopores after pretreated at each temperature; *filled circle*, mesopores after rewetted by boiling and dried by out-gassing at 50°C, using the same sample of *open circle* at 160°C after tested; *open squares*, micropores after pretreated at each temperature; *filled square*, micropores after rewetted by boiling and dried by out-gassing at 50°C, using the same sample of *open square* at 160°C after tested

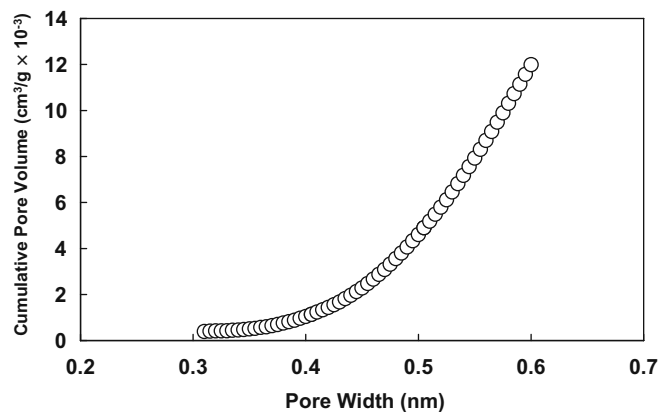


Fig. 4. Cumulative pore volume determined by the results of Fig. 2

mesopore analysis, to the results of Fig. 3. By using those methods, effects of pretreatment on micropore and mesopore volumes of dry wood were investigated.

Figure 6 shows the effects of pretreatment on cumulative pore volume of micropores and mesopores in the cell walls of dry wood. Pretreatments mean heat treatments by out-gassing at predetermined temperatures from 50° to 160°C

for 1 h just before the gas adsorption test. Drying and heating histories before pretreatments were almost the same between the samples. Thus, the difference in pore volume obtained should be considered to be affected only by the difference in pretreatments.

The micropore volume decreased with elevating pretreatment temperatures. In addition, to clarify whether the decrease in pore volume was a reversible change, the tested sample, which had been pretreated at 160°C, was boiled for 1 h and air-dried at room temperature for several days, and then dried by out-gassing at 50°C for 5 h and tested. The micropore volume of the sample pretreated at 160°C increased to the level of dry wood pretreated at 50°C by rewetting and drying (see Fig. 6). This result clarified that the decrease in micropore volume was a reversible change.

In contrast, mesopore volume hardly changed with increasing pretreatment temperatures. The tested sample

that had been pretreated at 160°C was boiled for 1 h and air-dried at room temperature for several days, and then dried by out-gassing at 50°C and tested. The mesopore volume of the sample was almost the same between before and after rewetting and drying (see Fig. 6).

From the foregoing results, it was concluded that micropores existed in the cell walls of dry wood and that the pore volume for micropores was ten times larger than that for mesopores when dried by out-gassing at 50°C. Furthermore, several physical phenomena that had been previously reported were also supportive for the existence of micropores in cell walls of dry wood: it has been reported that higher differential heat of adsorption was shown at lower moisture content¹⁵ and that swelling behavior of wood was not linear at lower moisture content.¹⁶ These phenomena can be explained by the reasons that moisture can adsorb onto dry wood without losing energy for breaking hydrogen bonds and that moisture adsorption at lower moisture content does not contribute to swelling of wood because of the existence of micropores. Judging from those past reports^{15,16} regarding to the physical properties of dry wood and the results in this report, it is considered to be reasonable that micropores exist in the cell walls in dry wood.

Comparison of micropore volume in the cell wall of dry wood between the softwood Hinoki and the hardwood Buna

In this study, it was revealed that a larger amount of micropores than mesopores existed in cell walls of dry wood. Thus, more information about micropores should be obtained here. Nakatani et al.^{7,17} reported that micropore volume decreased with the decrease in the residual lignin and suggested that micropores existed in the lignin in cell walls of dry wood from the results of adsorption of organic liquids and CO₂ gas. Focusing on the lignin from the results in the past study, micropore volumes of dry wood between softwood Hinoki and hardwood Buna were compared.

In Fig. 7, the dynamic viscoelastic properties of water-swollen softwood Hinoki and water-swollen hardwood Buna are compared. From the difference in the behavior of dynamic elastic modulus (E') and the peak temperatures of $\tan \delta$ between Buna and Hinoki, thermal softening temperature attributable to water-swollen lignin was considered to be lower for Buna than for Hinoki. This result agrees with past findings^{18–20} that hardwood lignins have lower softening temperatures than softwood lignins because of the difference in cross-linking, that is, the condensation level of lignin between softwood and hardwood. Figure 8 shows cumulative pore volumes of micropores for Hinoki and Buna. The micropore volume was larger for Buna than for Hinoki.

The degree of cross-linking, that is, condensation level, is reported to be lower with the hardwood lignin of Buna than with the softwood lignin of Hinoki. For this reason, larger amounts of micropores are considered to exist in the hardwood Buna than in the softwood Hinoki. In addition, this discussion corresponds to the result of the difference in thermal softening temperatures attributable to water-

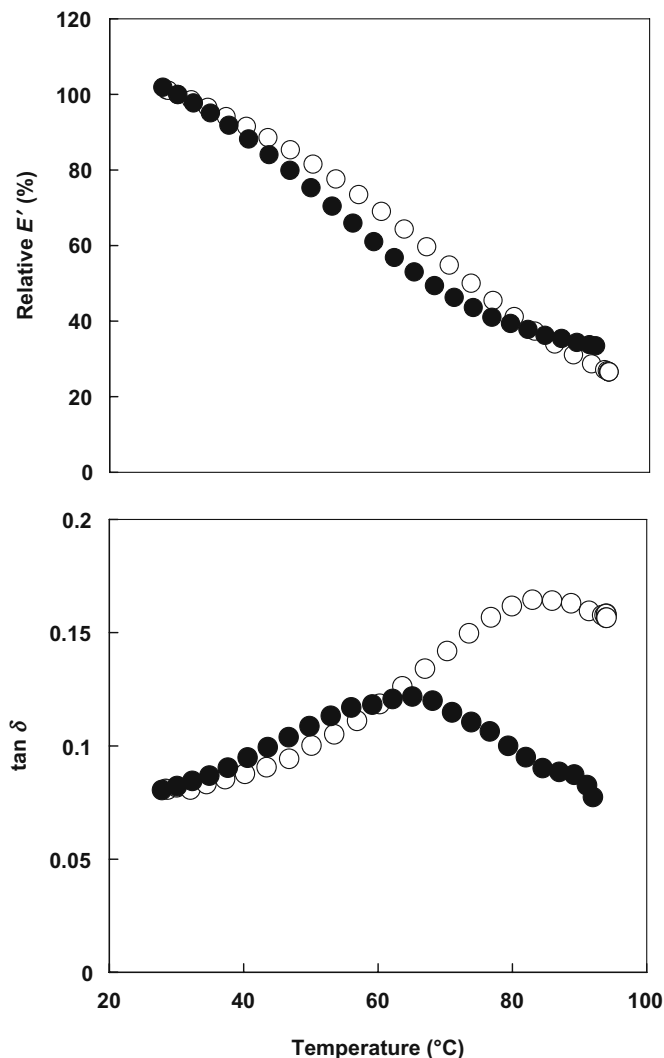


Fig. 7. Temperature dependence of dynamic viscoelastic properties of water-swollen softwood Hinoki and hardwood Buna at 0.05 Hz in the radial direction. *Open circles*, Hinoki; *filled circles*, Buna. Relative E' is relative to value at 30°C

swollen lignin between softwood Hinoki and hardwood Buna. The foregoing results in this report and the past report^{7,17} suggest that micropores in cell walls relate strongly to the structure of lignin.

Conclusions

To clarify the pore structure in cell walls of dry wood, the effects of heating history on pore volumes for both micropores and mesopores and the difference in pore volume between softwood Hinoki and hardwood Buna were investigated, using measurement of the gas adsorption of CO₂ at ice-water temperature (273 K) and of N₂ at liquid nitrogen temperature (77 K), as well as the measurement of dynamic viscoelastic properties. CO₂ gas adsorption isotherms obtained were used for determining micropore volumes smaller than 0.6 nm by the HK method,¹⁰ and N₂ gas adsorption isotherms obtained were used for determining

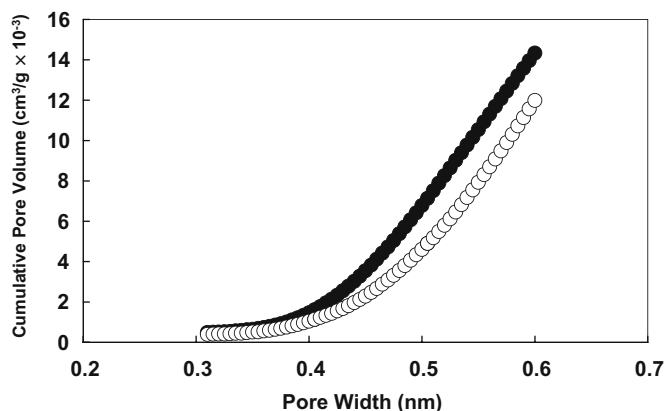


Fig. 8. Cumulative pore volume of micropores for the softwood Hinoki and the hardwood Buna determined by the gas adsorption of CO_2 at ice-water temperature (273 K) onto each sample after out-gassing at 50°C . *Open circles*, Hinoki; *filled circles*, Buna

mesopore volumes between 2 nm and 50 nm by the BJH method.¹⁴ Results obtained are as follows.

1. Micropores existed in the cell wall of dry wood for Hinoki, and the micropore volume was ten times larger than mesopore volume when dried by out-gassing at 50°C .
2. Micropores decreased with elevating pretreatment temperatures. The decreased micropore volume after heat treatment at 160°C returned to the level before heat treatment by rewetting and drying, so the decrease in micropore volume was a reversible change. On the other hand, mesopore volume hardly changed with elevation of pretreatment temperatures.
3. A larger amount of micropores existed in Buna (hardwood) than in Hinoki (softwood). The thermal softening temperature attributable to water-swollen lignin was lower for Buna than Hinoki. These results probably mean that micropores in cell walls relate to the structure of lignin, that is, the degree of cross-linking and condensation level of lignin.

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References

1. Nakato K (1973) Pore structure of wood (in Japanese). *J Soc Mat Sci Jpn* 22:903–907
2. Sawabe O, Mori K, Takeuchi T (1973) Micro-pore structure in cell wall of wood (in Japanese). *Mokuzai Gakkaishi* 19:55–62
3. Sawabe O, Kitagawa S (1978) Pore structure in swollen native cellulose: association with structural feature of native cellulose (in Japanese). *Mokuzai Gakkaishi* 24:164–170
4. Stone JE, Scallan AM (1965) Effect of component removal upon the porous structure of the cell wall of wood. *J Polym Sci Part C Polym Lett* 1:13–25
5. Stone JE, Scallan AM (1965) A study of cell wall structure by nitrogen adsorption. *Pulp Paper Mag Can* August:T407–T414
6. Akitomo M, Suzuki R, Ishimaru Y, Iida I, Furuta Y (2006) Micro-pore structure of wood and bamboo charcoals. Establishment of a method for the calculation of effective pore size distribution and the possibility of controlling micropore structure (in Japanese). *Mokuzai Gakkaishi* 52:228–234
7. Nakatani T, Ishimaru Y, Iida I, Furuta Y (2008) Micropore structure of wood: change in micropore distribution according to delignification. *J Wood Sci* 54:252–255
8. Kojiro K, Furuta Y, Ishimaru Y (2008) Influence of heating and drying history on micropores in dry wood. *J Wood Sci* 54: 202–207
9. Kojiro K, Furuta Y, Ohkoshi M, Ishimaru Y, Yokoyama M, Sugiyama J, Kawai S, Mitsutani T, Ozaki H, Sakamoto M, Imamura M (2008) Changes in micropores in dry wood with elapsed time in the environment. *J Wood Sci* 54:515–519
10. Harvath G, Kawazoe K (1983) Method for the calculation of effective pore size distribution in molecular sieve carbon. *J Chem Eng Jpn* 16:470–475
11. Struik LCE (1978) Physical aging in amorphous polymers and other materials. Elsevier, Amsterdam
12. Kojiro K, Furuta Y, Ishimaru Y (2008) Influence of heating history on dynamic viscoelastic properties and dimensions of dry wood. *J Wood Sci* 54:196–201
13. Furuta Y, Kojiro K, Nakatani T, Nakajima M, Ishimaru Y (2008) The dynamic viscoelastic properties of wood in nonequilibrium states (in Japanese). *J Soc Mat Sci Jpn* 57:338–343
14. Barrett EP, Joyner LG, Halenda PH (1951) The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J Am Chem Soc* 73:373–380
15. Stamm AJ, Loughborough WK (1935) Thermodynamics of the swelling of wood. *J Phys Chem* 39:121–132
16. Keylwerth R (1964) Investigations on free and restraint swelling of wood. Part IV: Investigations on the course of swelling and the dependence of wood density on moisture. *Holz als Roh- Werkstoff* 22:255–258
17. Nakatani T, Ishimaru Y, Iida I, Furuta Y (2008) Contribution of lignin on adsorption of organic liquids onto wood (in Japanese). *Mokuzai Gakkaishi* 54:17–23
18. Olsson AM, Salmen L (1992) Viscoelasticity of in situ lignin as affected by structure: softwood vs. hardwood. *J Am Chem Soc* 489:133–143
19. Higuchi T (1973) Chemistry of hardwood lignins. *Wood Res* 7:1–17
20. Furuta Y, Nakajima M, Nakatani T, Kojiro K, Ishimaru Y (2008) Effects of the lignin on the thermal-softening properties of the water-swollen wood (in Japanese). *J Soc Mat Sci Jpn* 57:344–349