J Wood Sci (2008) 54:515–519
DOI 10.1007/s10086-008-0973-5

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Changes in micropores in dry wood with elapsed time in the environment

Received: December 20, 2007 / Accepted: June 23, 2008 / Published online: October 6, 2008

Abstract To investigate the changes in microstructures of wood with elapsed time in the environment, CO_2 adsorption onto dry wood was measured at ice–water temperature (273 K) for samples aged from 0.1 years to over 1000 years. The micropore size distribution was obtained using the Horvath-Kawazoe method. Micropores smaller than 0.6 nm in wood decreased in number with elapsed time in the environment, and a negative correlation was found between cumulative pore volume for pores smaller than 0.6 nm and elapsed time in the environment. Cumulative pore volume in the 1000-year sample was almost half of that in the 0.1-year sample. Micropores smaller than 0.6 nm in wood with a few decades or more of elapsed time increased in number after rewetting and drying. Consequently, microstructures of wood with longer time elapsed in the environment were considered to be more stable, because of longer-term thermal motion and possibly more repeated moisture adsorption and desorption and/or temperature variation in the environment.

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Part of this report was presented at the 57th Annual Meeting of the Japan Wood Research Society, Hiroshima, August 2007

Key words Unstable state · Micropore structure · HK method · Old wood · Elapsed time

Introduction

It is well known that the properties of wood change over a long period in the environment after harvesting. Japan has many wooden buildings in temples and shrines that were built long ago. Studies about the changes in physical and mechanical properties with elapsed time have been conducted due to the importance of safe long-term use and as basic studies of wood science.[1–6]

Kohara[1,2] widely studied the physical and mechanical properties of old wood. It was reported that compressive strength, bending strength, and hardness of old wood from hinoki (*Chamaecyparis obtusa* Endl.), a softwood used in temple structures for over 1300 years, initially increased for a few hundred years and then decreased with time. The same properties of old wood from keyaki (*Zelkova serrata* Makino), a hardwood, decreased over a period of 650 years. Hirashima et al.[3–5] investigated the strength properties of old wood used in temple structures over a couple of hundred years, considering the effects of density, unlike Kohara's reports.[1,2] Compressive strength, modulus of elasticity, shearing strength, and static bending strength of old wood were larger for akamatsu (*Pinus densiflora* Siebold et Zuccarini), a softwood, and smaller for keyaki, a hardwood, than for both specimens of new wood, respectively. Tensile strength, impact strength, and hardness were not significantly different between old wood and new wood of akamatsu and keyaki, or tended to be smaller in old wood than in new wood of akamatsu and keyaki.[3–5] Interestingly, as mentioned above, many mechanical properties of softwood such as hinoki and akamatsu improved for a long time; however, the reason has not been clarified yet.

On the other hand, many recent studies[7–13] about the mechanical properties of wood in the unstable state, which is a state of transition to the thermodynamic equilibrium state, have been reported. Wood subjected to changes in

temperature and/or the 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. A similar phenomenon, called physical aging, is well known in various amorphous polymers,[14,15] and the phenomenon is explained by the free volume temporarily created by freezing molecular chain motion.

In previous reports,[16,17] we have attempted to clarify the influence of heating history on the dynamic viscoelastic properties and dimensions of dry wood, and the influence of heating on micropores of dry wood. Instability of dry wood still existed after heating at 105°C for 30 min and was modified by activated molecular motion in the first heating process to temperatures above 105°C, judging from larger dynamic elastic modulus (E') and smaller loss modulus (E'') in the second heating process than in the first heating process. Furthermore, to obtain more information about microstructures of dry wood having various heating and drying histories, adsorption of CO_2 was measured at ice–water temperature (273 K), and micropore size distribution was determined using the Horvath-Kawazoe method (HK method),[18] which is suitable for measuring micropore structures below 2 nm. It was revealed that the cumulative volume of micropores smaller than 0.6 nm in dry wood decreased with increasing heating temperature. This means that the instability of wood caused by drying is modified by more active molecular motion at a higher temperature, and it is expected to be more slowly modified at lower temperature, that is, in the environment. Therefore, if stabilization of the molecular chain in wood components occurs during the time elapsed in the environment, measuring the micropore volume is considered to be very effective for obtaining information about changes in the microstructure.

Accordingly, in this report, to obtain new information about changes in the microstructures of unstable wood exposed to the environment for a long period, the adsorption of CO_2 was measured at ice–water temperature (273 K) and micropore size distribution of old wood (long time elapsed after harvesting), was determined using the HK method. The results obtained were compared with the pore size distributions of new wood.

Materials and methods

Materials

Hinoki (*Chamaecyparis obtusa* Endl.) was used as the sample for measurement. The elapsed times after harvesting of the samples (samples A–O) are shown in Table 1. Samples E to O were collected from temples and a castle, such as Taimadera, Toshodaiji, and Horyuji[19] in Nara Prefecture, Senjuji[19] in Mie Prefecture, and Nijojo[19] in Kyoto Prefecture. Samples A to D were not used in buildings. Samples had different histories and different elapsed times in the environment, from 0.1 to about 1300 years. The elapsed times of samples E to O were determined from information such as existing old documents regarding the structures, and, in addition, for some samples, by dendrochronology and radiocarbon dating. Even if samples were obtained from the same structure, they had been used as different members in the structure and had different histories; therefore, samples with different labels were essentially different. Samples were obtained from parts of the structures that had not been directly exposed to the weather.

To measure CO_2 adsorption for the determination of pore-size distribution, the samples were cut into small cubes with edge lengths around 2 mm or smaller. Samples were used for measurements without any treatment after being conditioned in a room for several days at 20°C and 65% relative humidity (RH).

Methods

For analysis of the micropore structure, about 1 g of sample in the air-dried state was put into a sample cell for adsorp-

Table 1. Sample origin, elapsed time in the environment, and cumulative pore volume of pores smaller than 0.6 nm

Sample	Temple or castle · structure · member	Elapsed time (years)	Cumulative pore volume (cm^3/g)
A	Unused	0.1	0.0119
B	Unused	0.5	0.0107
C	Unused	8	0.0099
D	Unused	19	0.0096
E	Taimadera · Daishido · Uragouita	48	0.0068
F	Toshodaiji · Kondo · Hisashitenjyoketahagiki	109	0.0060
G	Toshodaiji · Kondo · Hashira	109	0.0079
H	Toshodaiji · Kondo · Keshouraita	314	0.0067
I	Senjuji · Mieido · Hashira	341	0.0062
J	Taimadera · Daishido · Uragouita	361	0.0062
K	Horyuji · Gojunoto · Hashira	392–411	0.0064
L	Nijojo · Komegura · Nuki	392–411	0.0058
M	Toshodaiji · Kondo · Nokikotenjokumiko	about 1220	0.0046
N	Toshodaiji · Kondo · Gagyo	about 1220	0.0041
O	Horyuji · Gojunoto · Taruki	1297–1415	0.0072

tion measurement of CO_2, and out-gassed for 5 h at 50°C under a high vacuum below 10^{-5} Pa. Pretreatment conditions were strictly the same among samples to equalize the effects of pretreatment history on the results. The amount of CO_2 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, using an automatic gas adsorption device AUTOSORB-1 (Quantachrome, USA).[20] The pore-size distribution of micropores smaller than 0.6 nm was determined using the HK method from the adsorption isotherms obtained.

Results and discussion

Influence of elapsed time in the environment on microstructures of dry wood

Physical and mechanical properties of wood are affected by histories such as temperature and/or swelling state, and microstructures of wood are considered to be strongly related to changes in those properties. In recent years, adsorption of CO_2 onto wood has been successfully measured at ice–water temperature (273 K) by Nakatani et al.[20] and Kojiro et al.[17] The latter reported that the number of micropores smaller than 0.6 nm in wood decreased with increasing heating temperature and were affected by the conditioning histories. When considering the relation of the unstable state to the microstructure of wood, investigating the micropore structure is very effective. Therefore, in this study, micropores in dry wood were measured with a similar method to that in the previous report, using samples with various elapsed times in the environment.

Micropore size distributions of dry wood

Figure 1 shows micropore size distributions determined by the adsorption of CO_2 with samples A, B, C, D, F, L, and O in Table 1, having various elapsed times in the environment. Samples in the air-dried state were dried by outgassing at 50°C for 5 h before adsorption measurements. Pore size distribution of pores smaller than 0.6 nm differed among samples with different elapsed time in the environment. Except for the result of sample O, pore volume within this range decreased with increased elapsed time in the environment. As shown in the previous report,[17] high reproducibility was obtained for similar measurements when the sample was conditioned in the same manner. Thus, differences in pore size distribution in Fig. 1 are considered to be attributable to differences in the microstructures of the measured samples.

When wood is dried, localized stresses are produced in the microstructure of wood components in cell walls. Instability of the microstructures of wood in the air-dried state is considered to still exist at around room temperature, because wood components in the air-dried state do not surpass their glass transition temperatures.[21] Immediately after drying, microstructures in wood are highly unstable,

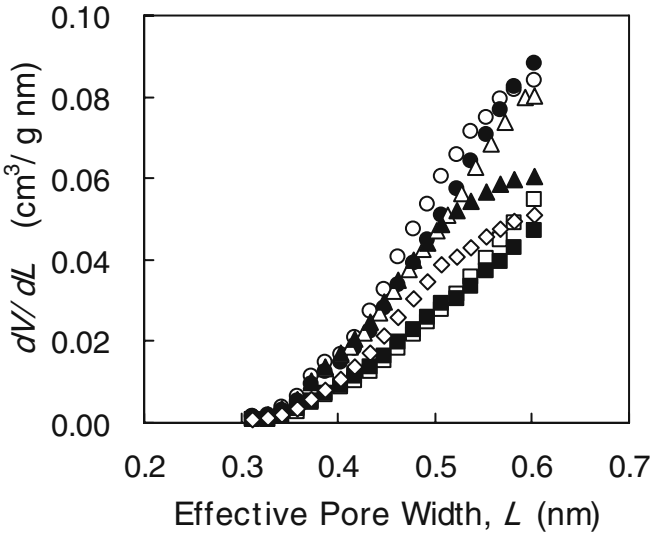

Fig. 1. Pore-size distributions determined by the adsorption of CO_2 at ice–water temperature (273 K) with samples A, B, C, D, F, L, and O. *Open circles*, sample A; *filled circles*, sample B; *open triangles*, sample C; *filled triangles*, sample D; *open squares*, sample F; *filled squares*, sample L; *open diamonds*, sample O

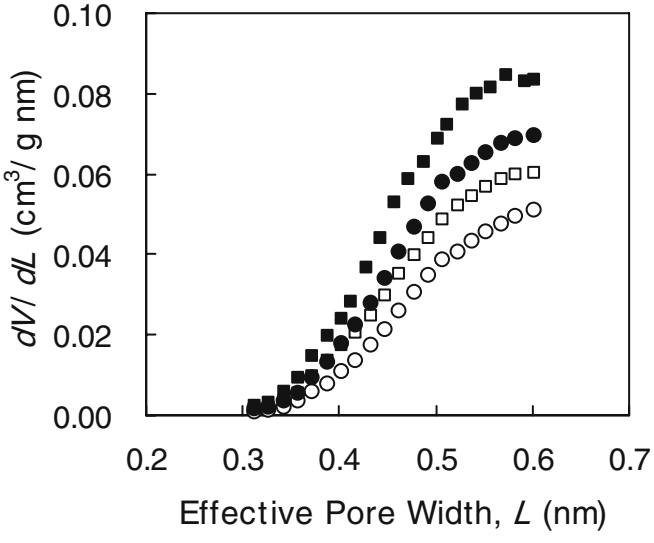

Fig. 2. Influence of rewetting and drying on pore-size distributions determined by the adsorption of CO_2 at ice–water temperature (273 K). *Open circles*, sample O; *filled circles*, sample O after rewetting and drying; *open squares*, sample D; *filled squares*, sample D after rewetting and drying

as judged from the result that wood immediately after drying had higher micropore volume than wood that experienced higher temperatures. A longer elapsed time in the environment is considered to make the microstructures in wood more stable, that is, with fewer micropores. If this deduction is correct, it is expected that the decrease in the number of micropores with elapsed time in the environment should be reversed after rewetting followed by drying.

Figure 2 shows micropore size distributions in the first measurements and the second measurements after rewetting and drying of samples D and O with elapsed times of

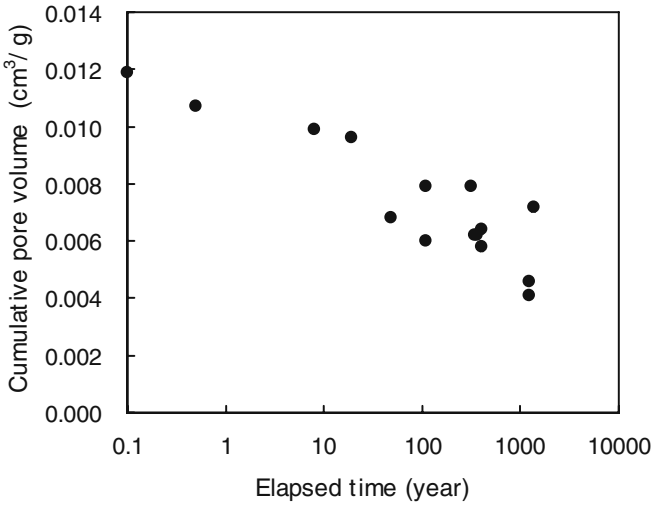

Fig. 3. Dependence of cumulative pore volume of micropores smaller than 0.6 nm on the elapsed time in the environment. See Table 1 for sample information

19 years and at least 1300 years in the environment, respectively. The samples were first measured after drying by out-gassing at 50°C for 5 h, and, after the measurements, the samples were boiled for 1 h and dried in a conditioned room (20°C and 65%RH) for several days. The samples were then second measured after drying by out-gassing at 50°C for 5 h. More micropores existed in samples D and O after rewetting and drying than in the first measurements. The number of micropores of sample D increased by rewetting and drying to a similar degree of pore volume for sample A with elapsed time of 0.1 years; however, the micropores of sample O did not recover so much by rewetting and drying. These results mean that elapsed time in the environment makes the microstructures in wood components more stable with fewer micropores, although micropores of wood with elapsed time of more than 1000 years do not return to the initial pore volume after harvesting, by rewetting and drying.

Cumulative micropore volume

In addition to micropore size distributions of samples with different elapsed time in the environment, cumulative pore volume should also be noted. Figure 3 shows the dependence of cumulative volume of micropores smaller than 0.6 nm, which was obtained from the result shown in Table 1, on elapsed time in the environment. In the range of elapsed time from 0.1 years to about 1300 years, a negative correlation was found between cumulative pore volume and elapsed time in the environment, although the data are spread to some degree. Moreover, judging from Fig. 3, cumulative pore volume of micropores smaller than 0.6 nm for the sample with elapsed time of about 1000 years in the environment was almost half of that for the sample with elapsed time in the environment for 0.1 years.

From the results above, it is clear that the volume of micropores smaller than 0.6 nm in wood decreases with elapsed time in the environment. This means that the microstructures of wood after longer elapsed times in the environment are more stable. This is attributable to the thermal motion of molecules of wood constituents for the long term and possibly to the repetition of adsorption and desorption of moisture and change in temperature making the microstructures of wood more stable than those of wood with less elapsed time in the environment. Therefore, improvement of the mechanical properties of wood with elapsed time is considered to partly result from stabilizing the microstructures of wood. In addition, considering the recent reports by Nakatani et al.[20,22] and the present result, changes in the microstructures of wood with elapsed time in the environment are considered to occur in lignin. However, to ascertain this, further investigation, including methodology such as the combination of spectrometry and measurement of viscoelastic properties, is needed.

Conclusions

Changes in the microstructures of dry wood with elapsed time in the environment were revealed by characterizing the micropore structures smaller than 0.6 nm from CO_2 adsorption at ice–water temperature (273 K). The results for samples aged from 0.1 years to about 1300 years are as follows.

Micropores smaller than 0.6 nm in wood decreased in number with elapsed time in the environment, and a negative correlation was found between cumulative pore volume for pores smaller than 0.6 nm and elapsed time from 0.1 years to about 1300 years in the environment. Cumulative pore volume for pores smaller than 0.6 nm in the 1000-year sample was almost half of that in the 0.1-year sample. The micropores increased in number by rewetting and drying. These results indicate that longer elapsed time in the environment makes the microstructures of wood more stable and decreases the number of micropores in wood, because of the thermal motion of molecules of wood constituents for the long term and possibly the repetition of adsorption and desorption of moisture and change in temperature.

Acknowledgments The authors express their gratitude, for the provision of the samples of old wood and helpful advice, to those affiliated with Taimadera and Toshodaiji in Nara Prefecture and Senjuji in Mie Prefecture, to the officials of the Nara Prefectural Board of Education, and to Dr. Haruko Sakai of the Nara Forest Research Institute.

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