ORIGINAL ARTICLE

Yutaka Ishimaru · Sigehiro Narimoto · Ikuho Iida

Mechanical properties of wood swollen in organic liquids with two or more functional groups for hydrogen bonding in a molecule

Abstract The modulus of elasticity and the modulus of rupture during static bending in the radial direction, and the viscoelastic properties in the radial direction in the temperature range 20°–100°C of hinoki (*Chamaecyparis obtusa*) swollen in organic liquids with two or more functional groups in a molecule were compared with those of wood swollen by moisture. The wood swollen in organic liquids in or near the swelling equilibrium, but not that swollen in organic liquids distant from the swelling equilibrium, showed higher moduli of elasticity and rupture than the wood swollen to a similar degree by moisture. This suggests that wood exists in an unstable state as it approaches the swelling equilibrium, rendering it highly flexible and weak. During the first viscoelastic measurements for wood swollen in various organic liquids, thermal softening was observed in 40°–60°C range and above 80°C, though this softening disappeared during the second measurement. The softening observed in the 40°–60°C range and above 80°C was thought to have been caused by the redistribution of liquid toward the equilibrium state at a higher temperature and the swelling accompanying an elevated temperature, respectively.

Key words Wood · Swelling · Organic liquid · Mechanical properties · Hydrogen bonding

Introduction

It has long been established that mechanical properties of wood vary with its moisture content.[1,2] In this regard, it has

Y. Ishimaru (✉) · S. Narimoto · I. Iida
Laboratory of Wood Technology, Faculty of Agriculture, Kyoto Prefectural University, Shimogamo Nakaragi-cho, Kyoto 606-8522, Japan
Tel. +81-75-703-5638; Fax +81-75-703-5639
e-mail: ishimaru@kpu.ac.jp

been reported that the mechanical properties of wood swollen in various organic liquids differ from those swollen to the same degree by moisture; i.e., the moduli of elasticity and rupture of wood swollen in organic liquids are generally higher than those of wood swollen by moisture. These differences in mechanical properties between organic liquid-swollen wood and moisture-swollen wood were attributable to the difference in the number of broken hydrogen bonds between molecules of the wood constituents, which is based on the difference in molecular sizes among the liquids, the differences in the adsorptive forces on wood constituents, and the differences in the cohesive forces among the liquid molecules.[3] Ishimaru et al. reported that the dynamic loss moduli of wood in various swelling states showed a close correlation to the modulus of rupture and explained this result using a simple viscoelastic model in which the mechanical properties of wood in various swelling states were related to the packing effect by the adsorption of the swelling liquids, differences in number of broken hydrogen bonds between the molecules of wood constituents, the cohesion forces of the liquids, the adsorption forces between the liquids and wood, and the temperature dependence of the latter two properties.[4] It has been reported that the swelling of wood in some liquids that have two or more functional groups in a molecule (even in those with a molar volume larger than 100ml/mol) exceeded the swelling induced by water,[5] although it had previously been thought that liquids with a molar volume larger than 100ml/mol could not swell wood.[6]

Based on these previous results, it was expected that we could obtain new information about the factors influencing the mechanical properties of wood swollen in various liquids. We therefore examined the mechanical properties of wood swollen in organic liquids with two or more functional groups in a molecule that are able to adsorb onto sites on the surface of fine voids in the cell walls. We were concerned with molecular dimensions, hydrogen bonding properties, and the number of functional groups of the liquids.

From this point of view, the modulus of elasticity and the modulus of rupture during static bending and the viscoelastic properties in the temperature range 20°–100°C

of wood swollen in some organic liquids with two or more functional groups in a molecule were compared with those of wood swollen by moisture. During the course of this investigation, some interesting findings were obtained regarding the temperature dependence of swelling and the mechanical properties of wood swollen in the organic liquids distant from the swelling equilibrium. These findings are discussed.

Materials and methods

Wood samples

Wood samples were obtained from the outer region of heartwood in a log of hinoki (*Chamaecyparis obtusa*). For swelling measurements, more than 65 cross-sectional wood pieces of 40 (R) × 20 (T) × 4 (L) mm were successively cut from a wood stick with a cross section of 40 (R) × 20 (T) mm. Their dimensions were measured in the tangential (T) and radial (R) directions with a precision of 0.01 mm by a screw micrometer after swelling in water (1 week at 30°C), vacuum drying (more than 50 h at room temperature), and oven drying (15 h at 105°C). The samples with abnormal shrinkage were discarded. These almost successive pieces were divided into 13 groups of five pieces each, and different groups were used to test swelling in the various liquids, by moisture, or after drying.

For measuring the static bending properties, 65 cross-sectional wood pieces of 100 (R) × 15 (T) × 4 (L) mm were successively cut from a wood stick with a cross section of 100 (R) × 15 (T) mm. The wood pieces were grouped in the same manner as described above for the swelling measurements.

For the measurement of viscoelastic properties, 65 cross-sectional wood pieces of 25 (R) × 4 (T) × 2 (L) mm were successively cut from a wood stick with a cross section of 25

(R) × 4 (T) mm. They were grouped as described above. All samples were stored in a desiccator containing dry calcium chloride until the next stage of treatment.

Organic liquids

The liquids used as swelling agents are listed in Table 1. The molecules of these liquids exhibit both proton-accepting and proton-donating properties. Diols and cellosolves have two functional groups per molecule, whereas ethereal oxygen increases with increasing molecular weight or with repeating units for the glycols. Organic liquids of the highest grade available and deionized and distilled water were used in all experiments without further purification.

Swelling of wood pieces in liquids

Nine groups of five pieces each for evaluating the nine swelling agents were placed in separate sample bottles, dried at 105°C for 15 h in an oven to avoid adsorption of moisture, and then immediately supplemented with one of the swelling agents listed in Table 1 under vacuum. Each sample bottle was sealed using a screw cap with Teflon liner packing. The samples were kept at constant temperature (20°C) for the previously reported durations[5] while attaining swelling equilibrium: 150 days for tetraethylene glycol, butanediol, and pentanediol; 90 days for the other organic liquids; and 30 days for water. After these periods the wood samples were removed from the bottles and subjected to measurements of the dimensions, static bending properties, and viscoelastic properties.

The dimensions of the tangential and radial directions of the wood pieces were measured to determine swelling. The degrees of swelling were evaluated from the cross-sectional swelling relative to that in water to eliminate variations among wood pieces.

Table 1. Swelling agents used

Swelling agent	Molar volume (ml/mol)	Cohesion energy density[a] (kJ/cm^3)	Chemical structure
Glycols			HO(C$_2$H$_4$O)$_n$H
Ethylene glycol (EG)	55.6	1.43	
Diethylene glycol (DEG)	94.9	1.19	
Triethylene glycol (TrEG)	133.4	1.16	
Tetraethylene glycol (TeEG)	172.7	1.18	
Diols			HOC$_n$H$_{2n}$OH
Propanediol (PrDO)	71.8	1.09	
1,4-Butanediol (BDO)	88.8	1.08	
Pentanediol (PnDO)	105.0	1.08	
Cellosolves			C$_n$H$_{2n+1}$OC$_2$H$_4$OH
Methyl Cellosolve (MC)	78.7	0.73	
Ethyl Cellosolve (EC)	117.3	0.61	
Water	18.0	2.31	HOH

[a] Calculated from the solubility parameter in a table by Hansen[7] for water and from data of boiling temperatures, enthalpies of evaporation, and molar heat capacities presented in a handbook of solvents[8] for organic liquids

Swelling by moisture

Two groups of wood pieces each were placed separately in a desiccator containing a saturated aqueous solution of ammonium sulfate [81.2% relative humidity (RH)[9]] and one of sodium carbonate hexahydrate (92.8% RH[9]). The desiccators were placed in a room regulated at 20°C for 1 month. These samples were then used for measurement of the dimensions, static bending, and viscoelastic properties.

Static bending test

The test samples prepared as described above were sealed using a polyethylene film prior to the test to avoid evaporation of the liquids and changes in moisture content. A testing machine for materials (Tensilon UTM-4L; Toyo Sokki, Japan) was used for the static bending test in the radial direction under the following conditions: span 80 mm of central loading and down-speed of a cross-head 4 mm/ min. The tests were stopped when the samples had broken down completely. Immediately after the test the wood samples were unsealed, and their width and thickness were measured. The modulus of elasticity (MOE) and the modulus of rupture (MOR) were calculated by conventional methods using the obtained stress–strain diagrams and dimensional data.

Measurement of dynamic viscoelastic properties

After measuring the width and thickness of the samples, the tests were performed in soaked states in the liquids or in silicon oil for the samples swollen by moisture and the dried samples, to avoid evaporation of the liquid and changes in the moisture content during the measurement. The dynamic modulus of elasticity (E') and dynamic loss modulus (E'') were measured in the radial direction by the tensile forced oscillation method (50 ± 40 g, 0.05 Hz) using an automatic viscoelastometer (TMS/SS 120; Seiko Instrument, Japan) at 20°–100°C (20°–90°C for the samples swollen in water and by moisture), increasing the temperature at a rate of 3°C/ min. After the first measurements, as described above, the samples were rapidly cooled with liquid nitrogen to about 20°C; the second measurements were then performed under the same conditions as used for the first.

Results and discussion

Swelling in the liquids

As described under Swelling of wood pieces in liquids, the swelling period for each liquid was determined by reference to our previous results.[5] Some of the liquids induced much less swelling in the present study than in our previous study. Mantanis et al. measured the rate of swelling in various liquids and found that the rate of swelling in liquids with large molecular sizes showed more dependence on
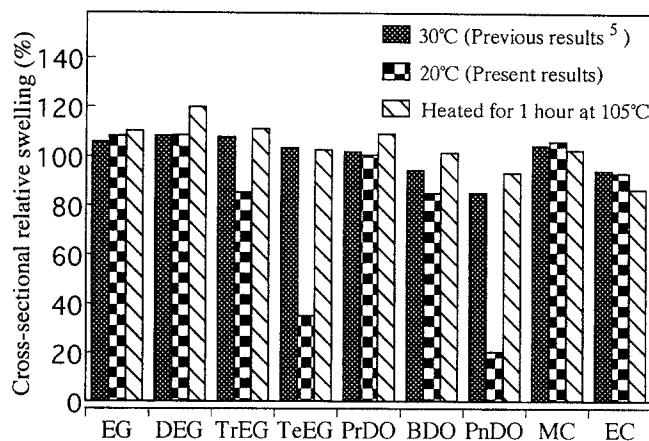

Fig. 1. Difference in cross-sectional relative swelling (cross-sectional swelling relative to that in water) among the samples swollen at different temperature conditions; swollen at 30°C and 20°C, and heated for 1 h after the measurement of the swelling at 20°C of swelling. *EG*, ethylene glycol; *DEG*, diethylene glycol; *TrEG*, triethylene glycol; *TeEG*, tetraethylene glycol; *PrDo*, propanediol; *BDO*, 1,4-butanediol; *PnDO*, pentanediol; *MC*, Methyl Cellosolve; *EC*, Ethyl Cellosolve

temperature.[10,11] The results should therefore be attributable to the difference in temperature during swelling periods (i.e., 20°C in the present study and 30°C in the previous study[5]). Moreover, it is possible that the swelling of samples changed during the visoelastic measurement in the temperature range 20°–100°C. Therefore, the soaked sample in each liquid whose dimension was measured at 20°C was placed in an oven at 105°C for 1 h. The dimensions of the samples were then measured again immediately after cooling to room temperature.

Figure 1 shows the cross-sectional relative swelling obtained in the previous[5] (30°C) and present (20°C) studies, and those measured after heating for 1 h at 105°C. The swelling in triethylene glycol (TrEG), tetraethylene glycol (TeEG), pentanediol (PnDO), and 1,4-butanediol (BDO) at 20°C was significantly less than that at 30°C. The swelling measured at 20°C in these liquids clearly did not approach the swelling equilibrium. In these cases, the rate of swelling was believed to have been strongly affected by the temperature difference of 10°C because of the relatively larger molecular size of the liquids. For the other liquids, in which the degree of swelling at 20°C was similar to that at 30°C, near-swelling equilibrium was assumed to have been attained. By elevating the temperature to 105°C for only 1 h, the swelling in TrEG, TeEG, propanediol (PrDO), and BDO increased extensively. This also indicates that the rate of swelling in these liquids was markedly influenced by temperature.

Comparing the swelling measured at 30°C and after elevating the temperature from 20°C to 105°C for 1 h, the degree of swelling of the heated samples was significantly larger than the swelling at 30°C in the case of diethylene glycol (DEG), PrDO, BDO, and PnDO. In the case of PnDO, it may have been due to the incomplete approach taken to the swelling equilibrium, but this would not have been the case for the other liquids because in these cases the

swelling was judged to be near the swelling equilibria from the previous results.[5] In contrast, the swelling in ethyl cellosolve (EC) was much less after heating than at 20°C. These results are believed to indicate not only that the rate of swelling strongly depends on temperature but that the equilibrium swelling depends on the temperature in a different manner among liquids.

Modulus of elasticity and modulus of rupture

The MOE and MOR of the wood samples treated in various ways are shown as a function of cross-sectional swelling in Fig. 2. The wood samples swollen in organic liquids, which can be considered to be almost at the swelling equilibrium, exhibit higher MOEs and MORs than those swollen to the same degree by moisture. This result is in accordance with the previous results[3] for wood swollen in liquids that have only one functional group in a molecule.

In the previous study,[3] the results similar to those described above were attributed to the difference among molecular sizes of liquids. That is, because the organic liquids used in both studies had molecular sizes larger than that of water, there were fewer hydrogen bonds broken in the wood swollen in the organic liquids than in the wood swollen to the same degree by moisture. Because of this, the

MOEs and MORs of the wood swollen in the organic liquids were larger than those of the wood swollen by moisture. This interpretation can be applied to the swelling seen in liquids that had two or more functional groups in a molecule.

In contrast with the above result, the wood samples swollen in TeEG and PnDO, which were distant from the swelling equilibrium, showed apparently lower MOEs and MORs than those swollen to the same degree by moisture. This result is notable in relation to the abnormal mechanical properties of wood under the nonequilibrium state of moisture, as it can be considered that wood exists in an unstable state as it approaches the swelling equilibrium, rendering it significantly weaker and more flexible than wood in the equilibrium state. In this connection, Furuta et al. found that the MOE of wood increases over the long term after soaking in water.[12]

In regard to the liquids that were in or near equilibrium, diols and cellosolves showed a decrease in swelling and an increase in MOE and MOR when the repeating units were increased from ethylene glycol (EG) to PrDO and from methyl cellosolve (MC) to EC, respectively. However, appreciable changes in swelling, MOE, and MOR accompanied by an increase in repeating units from EG to DEG were not observed for the glycols. These results are attributable to an increase in molecular size and to the number of functional groups participating in hydrogen bonding with the increase in repeating units. Morisato et al. reported that the adsorptivity of liquids onto wood, and therefore the swelling of wood in liquids, was basically determined by the balance of the energy generated by adsorption and the energy required for breaking the hydrogen bonds between wood constituents and for liberating liquid molecules from their cohesion states.[13] Accordingly, the above-mentioned results can be interpreted as follows. When the swelling decreased, the MOE and MOR increased owing to the increase in molecular size in the case of diols and cellosolves; in the case of glycols, however, the swelling and therefore the MOE and MOR did not change appreciably owing to both the increase in molecular size and the number of functional groups in a molecule.
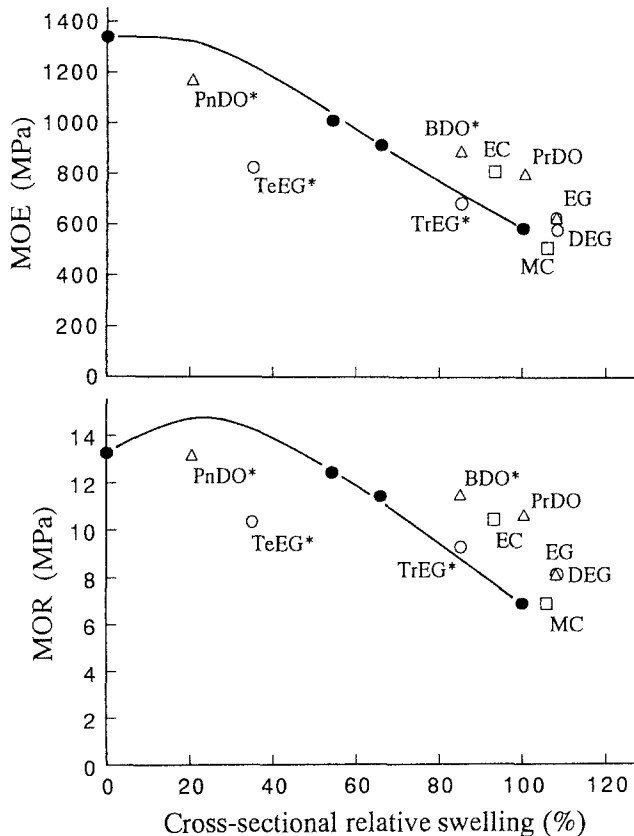
Dynamic MOE and dynamic loss modulus

Figures 3 and 4 show the changes in the dynamic MOE (E') and the changes in the dynamic loss modulus (E'') with temperature during the first set of measurements. Thermal softening regions (that is, abrupt decreases in E' accompanied by peak E'') were observed for all the wood samples, with the exception of dried wood, for which E' decreased almost linearly and E'' was relatively flat over the whole temperature region. There were few differences in the thermal softening regions among the swelling agents. Furthermore, in the case of PnDO and TeEG, which were far from the swelling equilibrium (Fig. 1), extensive decreases in E' and peaks of E'' are observed at relatively high temperature regions (>80°C). Such softening at relatively high temperatures was not observed for EG,

Fig. 2. Modulus of elasticity (*MOE*) and modulus of rupture (*MOR*) for bending in the radial direction as a function of cross-sectional relative swelling. *Swelling equilibrium not attained; *solid circles*, moisture conditioned; lines connected them are drawn by reference to the previous results[3]
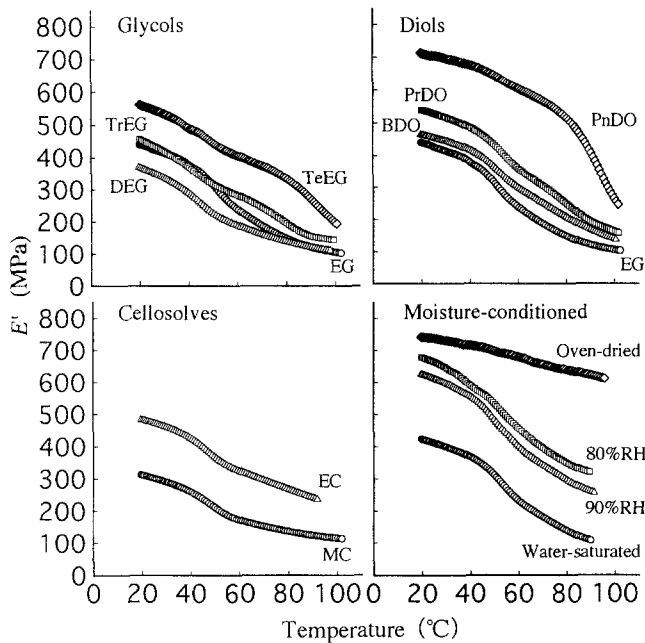
Fig. 3. Temperature dependence of dynamic modulus of elasticity (E') in the radial direction during the first measurement. RH, relative humidity in which wood samples were conditioned
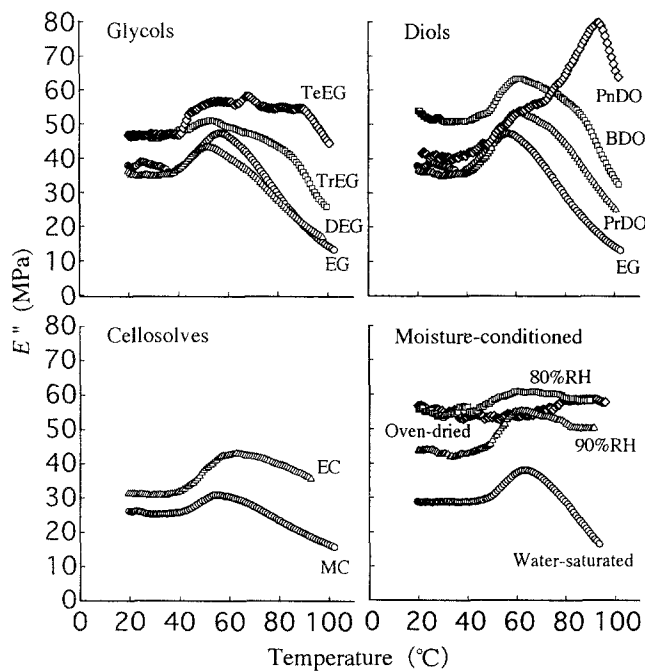

Fig. 4. Temperature dependence of dynamic loss modulus (E'') in the radial direction during the first measurement

Fig. 5. Elongation of the test pieces during the first viscoelastic measurement

DEG, or MC, in which the wood samples were close to attaining the swelling equilibrium.

The elongation of samples that showed typical dimensional changes during the first measurement are presented in Fig. 5. For PnDO and TrEG, in which wood samples were far from the swelling equilibrium and showed extensively increased swelling when the temperature was
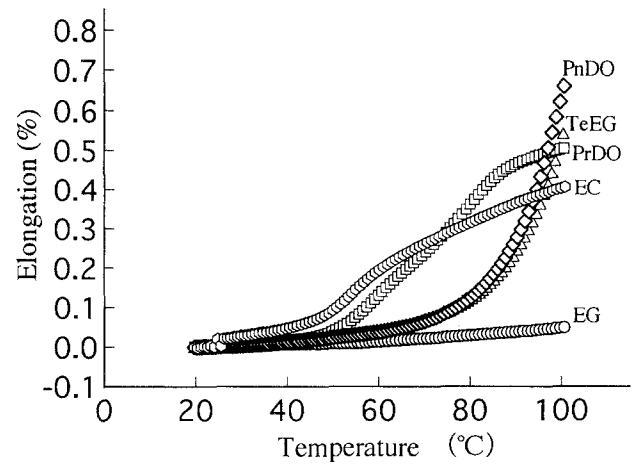
elevated to 105°C for 1 h (Fig. 1), extensive elongation was observed at temperatures corresponding to the thermal softening regions found in Figs. 3 and 4. Therefore, the elongation and thermal softening can be chiefly attributed to the increased swelling that accompanies the elevated temperature.

In the case of both PrDO and MC, in which the dimensions of the wood samples slightly increased or decreased, respectively, by elevating the temperature to 105°C, large elongations were observed at lower temperatures. These increases in dimensions were mainly attributable to creep deformation based on the similarity to the well known phenomenon that wood under nonequilibrium states of moisture exhibits an extensive increase in creep deformation.[14] In other words, this result means that creep deformation (i.e., fluidity) increases by both an increase and a decrease in organic liquids in wood in the same manner as in the case of the adsorption and desorption processes of moisture. Moreover, because the temperature regions where the deformation increase corresponded to the regions in which abrupt decreases in E' were found (Fig. 3), it is thought that the fluidity increase accompanied by increases and decreases in the amount of liquids in wood caused the abrupt decrease in E' during the first measurement.

For wood swollen in EG, although only a small amount of enlargement was observed during the first measurement, an obvious decrease in E' was found, as shown in Fig. 3. Furuta et al. found that Young's modulus of the wood soaked in water increases over 1 month with increasing soaking time; they explained that this result was due to the release of the strain caused by drying.[12] In any event, this result suggests that a longer exposure is necessary for the existing state of moisture in wood to reach the true equilibrium state, even if the swelling scarcely changes. The redistribution of moisture in wood toward the true equilibrium state should be accelerated by elevating the temperature; therefore, it can be interpreted that the increase in fluidity and the decrease in E' observed during
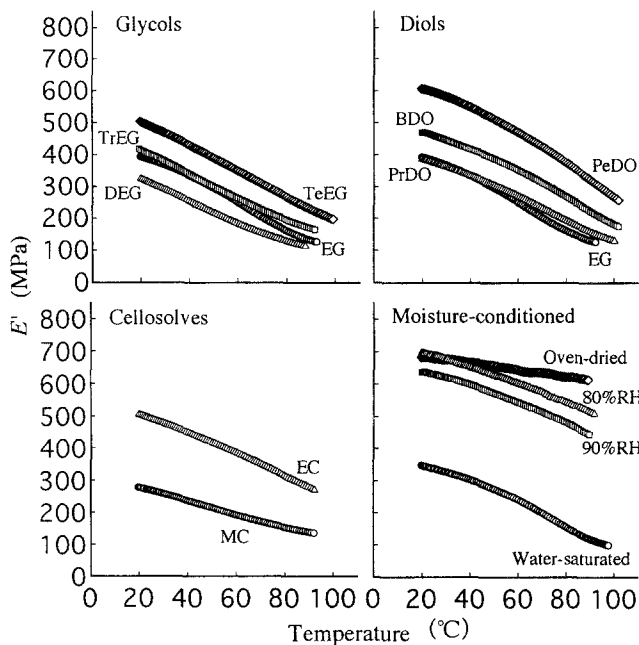
Fig. 6. Temperature dependence of dynamic modulus of elasticity (E') in the radial direction during the second measurement
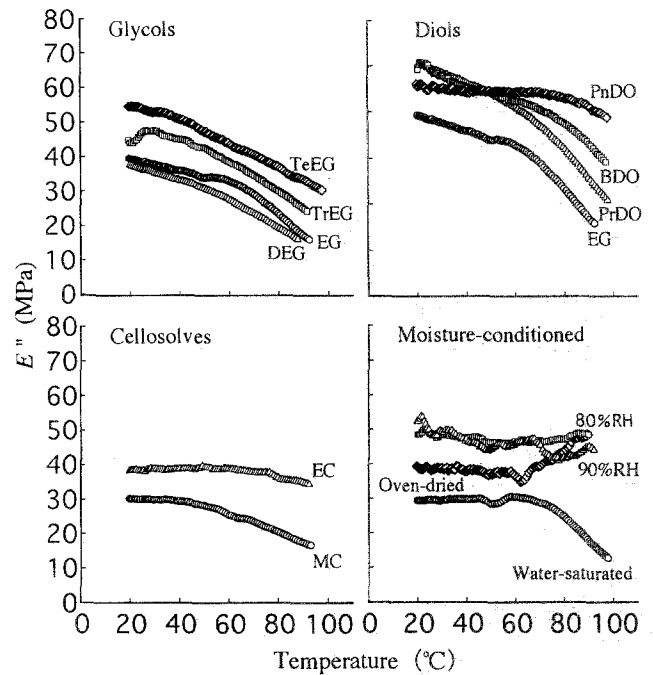

Fig. 7. Temperature dependence of dynamic loss modulus (E'') in the radial direction during the second measurement

this process occurred in a manner similar to that with the nonequilibrium states of moisture. It would then follow that the decrease in E' of the wood swollen in EG was attributable to the redistribution of EG molecules in wood. Moreover, the fact that the temperature regions of softening that are subtly different among swelling liquids can be explained by the differences in the temperature dependence of the adsorption force between the liquids and the wood constituents or the diffusion of liquid molecules in wood.

Figures 6 and 7 show the changes in E' and E'' with temperature during the second measurements using the same samples used for the first measurements. E' of all samples decreased almost linearly with temperature, and clear peaks of E'' were not found; that is, extreme thermal softening regions were not observed during the second measurement. A similar result was found for water-swollen wood and was attributed to the release of the strain produced by heating during the first measurement.[15] However, it is also possible to interpret it as due to the redistribution of liquid, mentioned above; that is, the true existing state of the swelling liquids in the equilibrium should vary with the temperature, with the liquids necessarily redistributing more easily toward the true existing state at higher temperatures. After rapid cooling following the first measurement, the liquids redistribute toward the true existing states only slightly at lower temperatures and so exist in an unstable state. During the second measurement, the redistribution of the liquid is less necessary because the liquid maintains the true existing state at higher temperatures. This may be the reason an obvious thermal softening region was not observed during the second measurement.

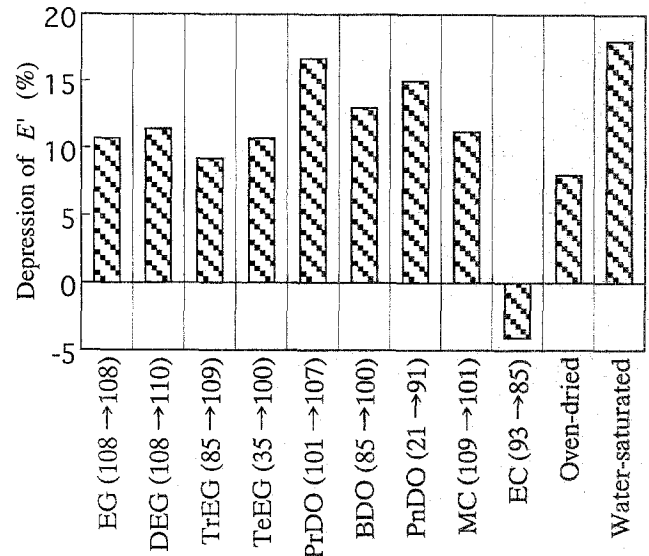Comparing E' at 20°C during the first measurement with that during the second (Figs. 3, 6), differences in E' are

Fig. 8. Depression of E' at 20°C as a result of cooling after the first measurement. Figures in parentheses indicate the changes in cross-sectional relative swelling caused by elevating the temperature from 20°C to 105°C for 1 h

observed. To compare these differences more distinctly, the depression of E' from the first to second measurement is shown in Fig. 8. Obvious depressions of E' are found for all the swollen wood samples and even for the dried wood samples with the exception of EC, in which the swelling significantly decreased when the temperature was elevated to 105°C for 1 h. A similar depression of Young's modulus was previously observed in the tangential and radial directions of the water-swollen wood, attributed to the strain produced by rapid cooling after the first

measurement.[12] The results obtained here show that such a phenomenon occurs not only for the wood swollen in various liquids but also for dried wood. Though the depressions for PnDO and TeEG were expected to be larger than those for the other liquids because of the significant increases in swelling, the difference was not as great as expected. This supports the above-mentioned hypothesis that the elasticity of wood in an unstable state toward the swelling equilibrium is smaller than that in the equilibrium state.

Conclusions

The rates of swelling of wood in organic liquids were strongly affected by temperature. It was suggested that equilibrium swelling depends on temperature differently among organic liquids. Appreciable changes in swelling MOE, and MOR accompanied by an increase in repeating units were not observed for glycols, though diols and cellosolves showed a decrease in swelling and an increase in MOE and MOR when the repeating units were increased. These results are attributable to the number of functional groups of glycols with increasing their repeating units. The wood swollen in organic liquids in or near the swelling equilibrium but not wood swollen in organic liquids distant from the swelling equilibrium showed higher MOEs and MORs than wood swollen to a similar degree by moisture. This suggests that the wood exists in an unstable state as it approaches the swelling equilibrium, rendering it highly flexible and weak. During the first viscoelastic measurements for wood swollen in various organic liquids, thermal softening was observed in 40°–60°C range and above 80°C, though this softening disappeared during the second measurement. The softening observed in the 40°–60°C range and above 80°C was thought to have been caused by the redistribution of liquids toward the equilibrium states at higher temperatures and the increased swelling that accompanies elevated temperatures, respectively. These results suggested that wood existing in an unstable state as it approaches the swelling equilibrium is highly flexible and weak.

References

1. Stamm AJ (1964) Wood and cellulose science. Ronald Press, New York, p 274
2. Kadita S, Yamada T, Suzuki M (1961) Study on rheological properties of wood. I. Effect of moisture content on the dynamic Young's modulus of wood (in Japanese). Mokuzai Gakkaishi 7:29–33
3. Ishimaru Y, Minase T (1992) Mechanical properties of wood in various stages of swelling. I. Mechanical and swelling behavior of wood swollen in various organic liquids (in Japanese). Mokuzai Gakkaishi 38:550–555
4. Ishimaru Y, Yamada Y, Iida I, Urakami H (1996) Dynamic viscoelastic properties of wood in various stages of swelling (in Japanese). Mokuzai Gakkaishi 42:250–557
5. Ishimaru Y, Maruta T (1996) Wood swelling and its transverse anisotropy in organic liquids having two or more functional groups in a molecule (in Japanese). Mokuzai Gakkaishi 42:234–242
6. Robertson AA (1964) Cellulose-liquid interaction. Pulp Paper Mag Can 65:T171–T178
7. Hansen CM (1967) The three dimensional solubility parameter: key to paint component affinities. J Paint Technol 39:104–117
8. Kuwata T (ed) (1967) In: Japan Association of Synthetic Chemistry of Organic Compounds: solvent pocket book, Yozai pocket book (in Japanese). Ohomu Sha, Tokyo, pp 479–485, 517–522, 531–532, 534, 559–561
9. Miyabe H (ed) (1968) In: Japan Society of Polymer Science: hand book of material and moisture [Zairyo to Mizu Handbook] (in Japanese). Kyoritu Shuppan, Tokyo, pp 240–262
10. Mantanis GI, Young RA, Rowell RM (1994) Swelling of wood. II. Swelling in organic liquids. Holzforschung 48:480–490
11. Mantanis GI, Young RA, Rowell RM (1995) Swelling of wood. III. Effect of temperature and extractives on rate and maximum swelling. Holzforschung 49:239–248
12. Furuta Y, Norimoto M, Yano H (1998) Thermal-softening properties of water-swollen wood. V. The effect of drying and heating histories (in Japanese). Mokuzai Gakkaishi 44:82–88
13. Morisato K, Ishimaru Y, Urakami H (1997) Adsorption of liquids and swelling of wood. III. Adsorption of some organic liquids onto dried wood (in Japanese). Mokuzai Gakkaishi 43:986–992
14. Tokumoto M (1994) Creep and set of wood in the non-equilibrium states of moisture (in Japanese). Mokuzai Gakkaishi 40:1157–1164
15. Furuta Y, Yano H, Norimoto M (1998) Thermal-softening properties of water-swollen wood. I. The effect of drying history (in Japanese). Mokuzai Gakkaishi 41:718–721