ORIGINAL ARTICLE

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Vapor phase reaction of wood with maleic anhydride (II): mechanism of dimensional stabilization

Abstract The vapor phase reaction of wood with maleic anhydride (MA) was investigated from the aspect of the mechanism of dimensional stabilization. Notably the existence of cross-links was examined by detailed analyses of dimensional stability and related properties, diffuse reflectance infrared Fourier transform (DRIFT) spectra, and changes in mechanical properties such as creep property and vibrational property. Higher reaction temperature resulted in less leaching of reagent. Also a peak in DRIFT spectra at $1730\,cm^{-1}$ showed the esterification of wood components with MA, while that at around $1780\,cm^{-1}$, which became remarkable with increasing reaction temperature, suggested the formation of cross-linking. The loss tangent decreased and the creep deformation was restrained for the specimens treated at high temperature. From these results it is plausible that MA mainly forms monoester with wood components at lower temperature; however, at elevated temperature cross-linking appears in addition to formation of the monoester.

Key words Creep property · Dimensional stability · Maleic anhydride · Vapor phase reaction · Vibrational property

Introduction

Satisfactory dimensional stability and excellent antifungal properties have been achieved by vapor-phase reaction of wood with maleic anhydride (MA) without marked increase in the bulking coefficient (B). Furthermore, when the reaction has been carried out at elevated temperature (180°C), the leaching of reagent and the accompanying lowering of the antiswelling efficiency (ASE) were restrained, and the formation of cross-links was suggested.[1]

In this article, the mechanism of dimensional stabilization and the changes of mechanical properties are discussed in connection with the reaction temperature. Notably, the existence of cross-links is examined. To date various chemical modifications of wood have been correlated with mechanical properties such as creep property,[2,3] vibrational properties,[4] and so on. They stated that the creep deformation is restrained and loss tangent (tan δ) decreases significantly when rigid cross-links are formed between wood components: such is the case for formaldehyde treatment in the vapor phase. Furthermore, Yasuda et al.[5–7] have also referred to the relationship between cross-linking and changes of mechanical properties. They found extreme resistance to creep deformation and a decrease of tan δ for some chemical modifications in which cross-linking is speculated to occur.

Analyses of dimensional stability in association with moisture-excluding effects, diffuse reflectance infrared Fourier transform (DRIFT) spectra, and changes in mechanical properties may offer information concerning the mechanism of dimensional stabilization (e.g., existence of cross-linking).

Materials and methods

Wood samples and reagent

Specimens were cut from sapwood of sugi (*Cryptomeria japonica* D. Don). For the evaluation of dimensional stability, six matched specimens, 28 (T) × 28 (R) × 5 mm (L), were assigned for each reaction condition. The same size specimens were then treated for DRIFT spectroscopy. For vibrational property and mechanosorptive creep tests, three specimens, 2 (T) × 12 (R) × 150 mm (L), were prepared for each reaction condition.

All specimens were dried under vacuum at 60°C for 48 h, weighed, and measured. Then they were conditioned over a

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saturated aqueous solution of potassium acetate in a desiccator at 20°C until their moisture content had equilibrated with the relative humidity (ca. 22.8%).

Reagent grade maleic anhydride (MA) (Wako, Osaka) was used.

Vapor phase reaction with MA

Six specimens for the evaluation of dimensional stability, three for mechanical property tests and three for DRIFT spectroscopy (total oven-dried weight: ca. 16 g), and MA (2.785 g) were placed in a 6.7-l glass vessel preheated to the reaction temperature. The vessel was evacuated once and heated in an oven for 24 h. The internal pressure of the vessel was about 7 hPa, when it was evacuated without anything. The weight ratio of available MA to wood was 17.5:100. The concentration of MA in the vapor phase was estimated to be about 4.2×10^{-3} mol l^{-1} under the assumption that MA vaporizes completely and behaves as an ideal gas. At the end of the heating process, atmospheric pressure was restored in the vessel and the whole vessel was allowed to cool for about 1.5 h. The specimens were heated in an oven at 105°C for 72 h to remove unreacted MA. The weight increase (WPG) was calculated from the oven-dried weight before and after treatment. Bulking coefficient (B) was defined as follows,

$$B(\%) = \frac{a_1 - a_0}{a_0} \times 100 \tag{1}$$

where a_0 and a_1 are the oven-dried cross-sectional area before and after treatment, respectively. Some specimens were prepared by a similar manner without MA.

Evaluation of dimensional stability and moisture-excluding effect

Both treated and untreated specimens were conditioned at 20°C and 92% relative humidity (RH) for about 1 month. The antiswelling efficiency in the conditioned state (ASE$_m$) was defined as follows,

$$\text{ASE}_m(\%) = \frac{S_m^u - S_m^t}{S_m^u} \times 100 \tag{2}$$

where S_m^u and S_m^t are the swelling coefficients for the cross-sectional area between the oven-dried and conditioned states for untreated and treated wood, respectively. The S_m^t was defined by

$$S_m^t(\%) = \frac{a_2 - a_1}{a_1} \times 100 \tag{3}$$

where a_1 is the oven-dried cross-sectional area after treatment, and a_2 is the cross-sectional area after conditioning.

The reduced moisture-excluding efficiency (MEE$_R$) was defined by

$$\text{MEE}_R(\%) = \frac{M^u - M_R^t}{M^u} \times 100 \tag{4}$$

where M^u is the moisture content of untreated wood, and M_R^t is the reduced moisture content of treated wood calculated by

$$M_R^t(\%) = \frac{w_2 - w_1}{w_0} \times 100 \tag{5}$$

where w_0 is the oven-dried weight before treatment, and w_1 and w_2 are the oven-dried and conditioned (20°C, 92% RH) weights after treatment, respectively.

The antiswelling efficiency in a water-saturated state (ASE$_w$) was calculated using a similar equation to Eq. 2. In this case, the swelling was estimated by the change in cross-sectional area between the oven-dried and water-saturated states at 20°C. The reduced reduction in water absorptivity (RWA$_R$) was defined as follows,

$$\text{RWA}_R(\%) = \frac{W^u - W_R^t}{W^u} \times 100 \tag{6}$$

where W^u is the water absorption of untreated specimen, and W_R^t is the reduced water absorption for a treated specimen. The latter can be calculated using the oven-dry weight before treatment (w_0) and the oven-dried (w_1) and water-saturated weight (w_3) after treatment as follows,

$$W_R^t(\%) = \frac{w_3 - w_1}{w_0} \times 100 \tag{7}$$

The water soaking (attained by dipping in water for 2 h at 40 hPa, 2 h at 1.37 MPa, and 24 h at ambient pressure) and oven drying (50°C for 24 h and 105°C for 24 h) were repeated three more times. Both ASE$_w$ and RWA$_R$ were evaluated each time.

DRIFT spectroscopy

A Shimadzu FT-IR 8200PC was used for DRIFT spectroscopy. Wood meal that was passed through a 74-μm screen was diluted one fortieth by weight with KCl.[8] The spectrum of neat KCl was adopted as a background. All spectra were the signal average of 200 scans, with a resolution of 4.0 cm^{-1}.

Determination of vibrational properties

After being conditioned at 20°C and 65% RH for 3 weeks, the specimens were subjected to a vibrational property test using the free–free flexural vibration method. Specific dynamic Young's modulus (E/γ) in the longitudinal direction was calculated from the resonance frequency of the first vibrational mode. Meanwhile, tan δ was obtained from the damped oscillation curve just after unloading the vibration. The measurement was conducted before and after treatment for each specimen.

Mechanosorptive creep test

The mechanosorptive creep test was carried out according to Yasuda et al.[7] at 30°C with three-point bending (span length 100mm). The relative humidity was elevated from 53% to 85% just after adding the 10MPa load. After 24h, the humidity was lowered to 53% RH, which was maintained for 1 day, and then the load was removed. The deflection was monitored by means of a laser displacement meter.

The degree of creep deformation was standardized by the anticreep efficiency (ACE)[2] defined by

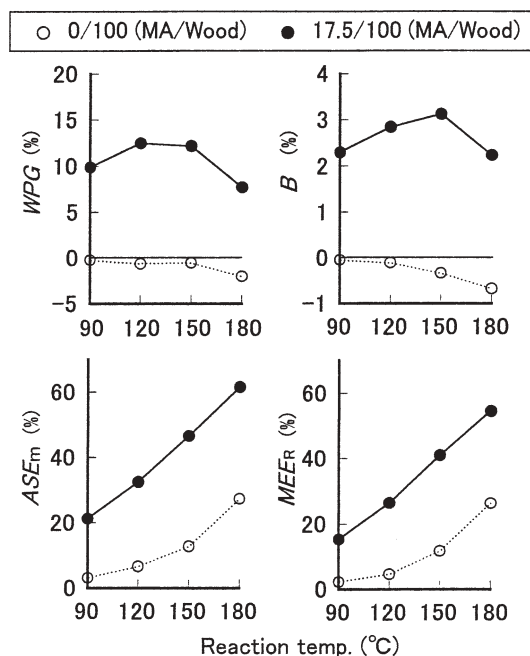$$ACE(\%) = \frac{dJ^u - dJ^t}{dJ^u} \times 100 \quad (8)$$

$$dJ = \frac{4bh^3}{Fl^3}(y_2 - y_1) \quad (9)$$

where dJ^u and dJ^t are the creep compliances of untreated and treated specimens, respectively, F is the applied load, y_1 is the deflection just after loading, y_2 is that just before unloading, l is span length, and b and h are width and thickness of the specimen, respectively.

Results and discussion

Dimensional stability and related properties

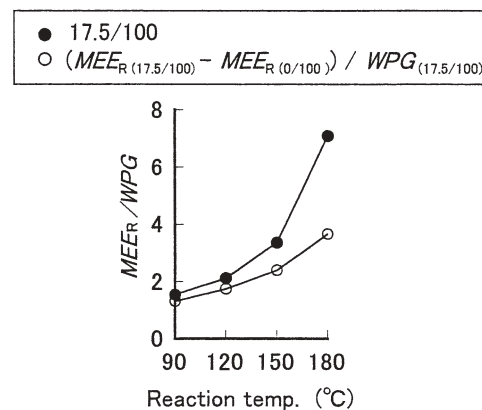Figure 1 shows the dependence of WPG, B, ASE_m, and MEE_R on the reaction temperature. WPG and B did not depend on the temperature. On the other hand, ASE_m and MEE_R increased with the rise in the reaction temperature, and a good correlation can be expected between these two properties, which implies that dimensional stabilization arises mainly from a reduction of hygroscopicity.

Figure 2 shows that the MEE_R/WPG ratio was especially high at 180°C. Although the MEE_R increases with simple heating at an elevated temperature, this tendency was weak even after subtracting the thermal effect. These results suggest that the amount of MA taken up in the cell walls depends little on the reaction temperature, whereas the modes of linkage with wood components depend strongly on the temperature.
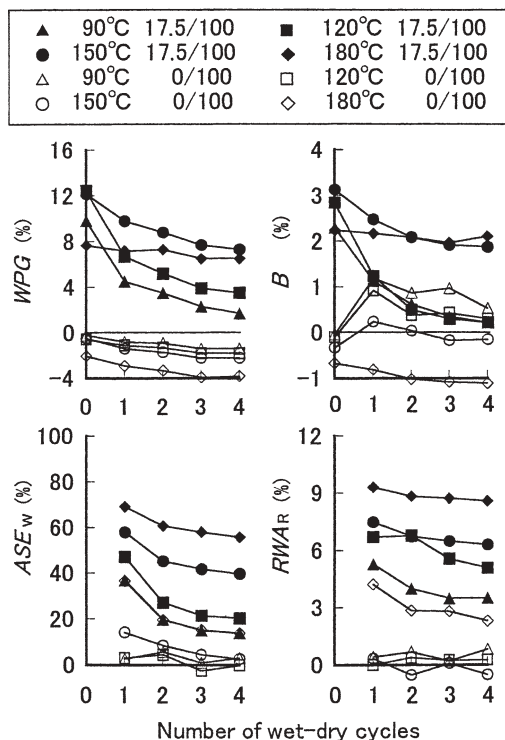
Figure 3 shows the changes of WPG, B, ASE_w, and RWA_R with repeated water soaking. The leaching of reagent was suppressed, and ASE_w and RWA_R were maintained much better when the reaction was carried out at high temperature, especially at 180°C where the WPG and B hardly decreased at all. At high temperature, dimensional stabilization may occur via some other mechanism (e.g., formation of cross-links).
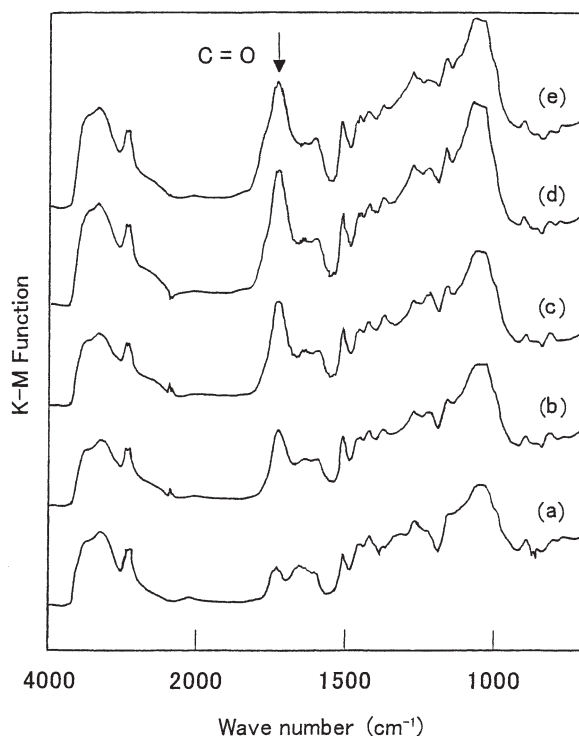
DRIFT spectrum of MA-treated wood

Figure 4 shows the DRIFT spectra for MA-treated wood. A peak observed for each reaction temperature at around 1730 cm^{-1} can be assigned as the carbonyl absorption band due to the maleic acid ester.[9] This suggests the esterification of hydroxyl groups in wood components. When subtracting the thermal effect for every reaction temperature, a shoulder peak appeared at around 1780 cm^{-1} and increased with rising reaction temperature (Fig. 5). This is attributable to the stretching of the C=O group from the conjugated, noncyclic acid anhydride and/or saturated lactone.[9] Such an acid anhydride may occur as a result of dehydration between the carboxyl groups coming from the monoester between MA and wood components. On the other hand, a saturated lactone may be formed by a radical reaction between the double bond of maleic acid and wood components. These forms of bonding are no less a kind of cross-linking. Because radicals are likely to occur in wood
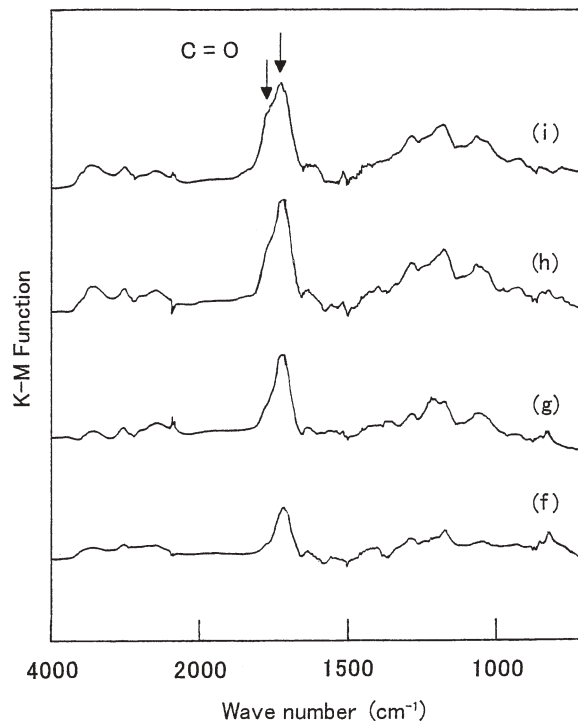

Fig. 1. Dependence of weight increase (WPG), bulking coefficient (B), antiswelling efficiency in the conditioned state (ASE_m), and reduced moisture-excluding efficiency (MEE_R) on the reaction temperature. Initial moisture content: 4.5%; reaction condition: each reaction lasted 24h. *MA*, maleic anhydride

Fig. 2. Dependence of MEE_R/WPG ratio on the reaction temperature

Fig. 3. The changes of WPG, B, antiswelling efficiency in water-saturated state (ASE_w), and reduced reduction in water absorptivity (RWA_R) with repeated wetting and drying

Fig. 5. Difference in DRIFT spectra between wood samples treated with and without MA. Conditions: 90°C 17.5/100 − 90°C 0/100 (*f*); 120°C 17.5/100 − 120°C 0/100 (*g*); 150°C 17.5/100 − 150°C 0/100 (*h*); 180°C 17.5/100 − 180°C 0/100 (*i*). *Arrows* indicate carbonyl absorptions

Fig. 4. Comparison of the diffuse reflectance infrared Fourier transform (DRIFT) spectra of untreated wood (*a*), 90°C 17.5/100 (*b*), 120°C 17.5/100 (*c*), 150°C 17.5/100 (*d*), 180°C 17.5/100 (*e*)

components at elevated temperature, cross-linking due to radical reaction may increase at 180°C. Silverstein et al.[9] claimed that the C=O stretching absorption band shifts to a higher wavenumber in the spectra of vinyl or phenyl ester, each of which have an unsaturated moiety next to the C=O group. Therefore, if the C=O is introduced to the phenyl group of lignin by esterification, a similar situation is likely. It has also been proved by differential scanning calorimetry (DSC) that MA reacts with lignin–hemicellulose matrix at 150°C.[10]

The ratios of absorbance at 1728 and 1778 cm^{-1} (due to C=O in maleic acid ester, conjugated noncyclic acid anhydride, and saturated lactone) to that at 1510 cm^{-1} (due to the aromatic ring),[11] and the ratios divided by WPG were plotted against reaction temperature (Fig. 6). The peak ratio divided by WPG tends to increase with a rise in the reaction temperature, and was especially high at 180°C for both absorbance peaks. This is in agreement with the result shown in Fig. 2, where MEE_R/WPG increases with the reaction temperature, and suggests that the esterified wood components and cross-linking contribute to the moisture-excluding effect.

Vibrational property

The values for E/γ and tan δ are summarized in Table 1 along with specific gravity (γ), WPG, moisture content (M) in the conditioned state, and reduced moisture content of treated wood (M_R^t). Figure 7 illustrates the relationship

Table 1. Vibrational properties

Reaction temperature (°C)	MA/wood[a]	γ	WPG (%)	M (%)	M_{R}^{t} (%)	$E/\gamma \times 10^{-10}$ (Pa)	$\tan \delta \times 10^{3}$
90	0/100	0.41	−0.3	10.3	10.4	2.38 (0.979)	6.01 (0.980)
90	17.5/100	0.39	5.8	8.2	8.8	2.37 (0.971)	7.51 (1.244)
120	0/100	0.41	−0.1	10.1	10.1	2.52 (0.990)	5.87 (0.995)
120	17.5/100	0.41	8.6	6.9	7.5	2.38 (0.978)	7.30 (1.218)
150	0/100	0.38	−1.4	9.1	9.0	2.56 (1.015)	5.74 (0.935)
150	17.5/100	0.42	9.6	5.4	5.9	2.51 (0.983)	6.15 (1.011)
180	0/100	0.36	−2.6	7.7	7.5	2.68 (1.027)	5.56 (0.919)
180	17.5/100	0.41	5.4	4.9	5.2	2.42 (0.959)	5.23 (0.869)
Untreated	–	0.39	–	11.1	–	2.51 (–)	6.08 (–)

Values in parentheses were obtained from treated/untreated wood. Initial moisture content was 4.5%; each reaction lasted 24 h
MA, maleic anhydride; γ, specific gravity; WPG, weight increase; M, moisture content at 20°C and 65% relative humidity (RH); M_{R}^{t}, reduced moisture content at 20°C and 65% RH; E, Young's modulus
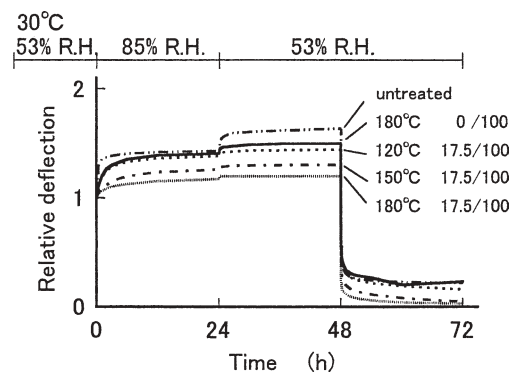[a] The weight ratio of MA to total oven-dried weight of untreated specimens
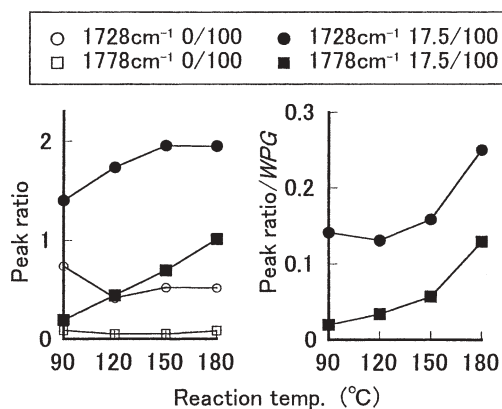
Fig. 6. Dependence of peak ratio (Carbonyl signal at 1728 or 1778 cm^{-1}/aromatic signal at 1510 cm^{-1}) and that divided by WPG on the reaction temperature
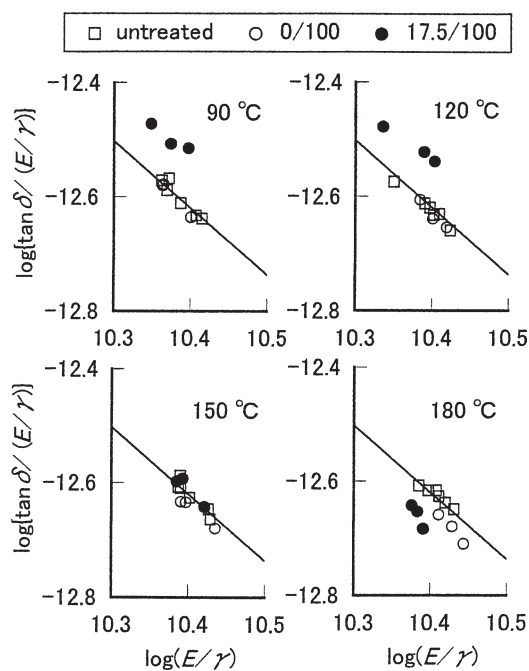
Fig. 7. Relationship between log (E/γ) and log [tan $\delta/(E/\gamma)$]. *Solid line*, regression line for untreated specimens


Fig. 8. Relative deflection with time elapsed in the bending creep test

between the logarithm of E/γ and that of tan δ. It is generally known that a linear correlation is observed between these parameters for untreated wood,[12–14] but after treatment the plot deviates from the line because of the change in molecular structure in the amorphous region of the cell wall.[4] In this study, tan δ shifted above the regression line for untreated wood when treated at low temperature, but the reverse was true when treated at high temperature. The state of MA in the cell wall may differ depending on the reaction temperature. Because tan δ should decrease as a result of the decrease in slippage between molecular chains, cross-linking probably occurs when the reaction is carried out at an elevated temperature. However, the decrease in tan δ (13.1%) is not as significant as that after formaldehyde, glyoxal, and glutaraldehyde treatments (30% or more), where cross-linking is known to occur. Therefore, the formation of cross-links is not always clear in the case of MA treatment.

Creep property

Figure 8 shows the profile of the deformation in the bending creep test. The higher the reaction temperature, the less pronounced was the deformation. In Fig. 9, the ACE of MA treatment was compared with that of chemical treatments cited by Norimoto et al.[2] and Yasuda et al.[7] When MA
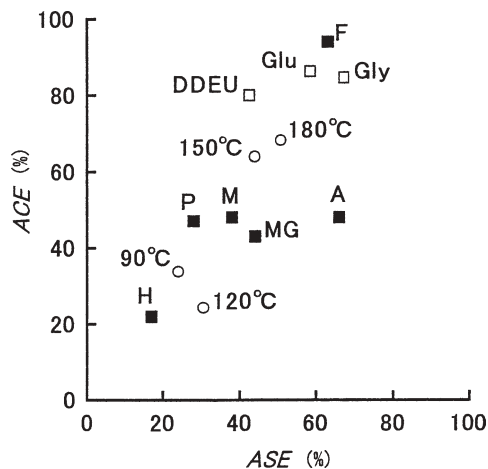
Fig. 9. Relationship between anticreep efficiency (ACE) and ASE. *Open circles*, obtained in this study; *filled squares*, cited from Norimoto et al.[2]; *open squares*, cited from Yasuda et al.[7]; *F*, formalization, vapor phase, catalyst SO$_2$; *A*, acetylation; *M*, maleic acid impregnation; *MG*, maleic acid and glycerol impregnation; *P*, phenolic resin impregnation; *H*, heat treatment (180°C); *Gly*, glyoxal impregnation; *Glu*, glutaraldehyde impregnation; *DDEU*, 4,5-dihydroxy-1,3-bis(hydroxymethyl)imidazolidin-2-one impregnation

treatment was carried out at high temperature, the ACE was as high as that for formaldehyde, glyoxal, and glutaraldehyde treatments in which cross-linking is possible. Moreover, the ACE attained by MA treatment at high temperature is much higher than that for other treatments such as acetylation where cross-linking is improbable. From these results, it is deduced that cross-links are formed when MA treatment is carried out at 150°C or higher.

Conclusions

The reaction of wood with MA was carried out in the vapor phase at different temperatures. When the reaction was conducted at high temperature, the MEE$_R$/WPG ratio increased, and leaching of reagent was restrained. In the DRIFT analysis, an absorption peak appeared at 1730 cm^{-1}, which showed the esterification of wood components with MA. Notably, the peak intensities at 1730 and 1780 cm^{-1} increased with rising temperature. The increase of the former peak suggests the formation of cross-linking by diester, while that of the latter peak suggests cross-linking by dehydration between carbonyl groups and/or radical reactions. The tan δ value decreased and creep deformation was restrained for the specimens treated at high temperature.

From these results, it is plausible that at lower temperature MA tends to form a simple monoester with wood components, whereas cross-linking becomes remarkable at elevated temperature.

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