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Vapor phase reaction of wood with maleic anhydride (I): dimensional stability and durability of treated wood

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Abstract Reaction between maleic anhydride (MA) and wood specimens was carried out in a vapor phase reaction system. Reaction conditions such as the ratio of supplied MA to wood, initial moisture content, and reaction temperature were optimized. The MA supplied to the reaction system was effectively absorbed by the wood, and a satisfactorily high dimensional stability was achieved even at a low MA/wood ratio. The dimensional stability increased with rising initial moisture content. When the reaction was conducted at an elevated temperature (180°C), high dimensional stability was attained without remarkable weight increase and bulking. The mechanism of dimensional stabilization was discussed on the basis of the dimensional changes at high humidity and during repeated water soaking and drying. It was shown that the dimensional stabilization arises mainly from a decrease of hygroscopicity. When the reaction was conducted at 180°C, the formation of cross-links in the cell wall was apparent. Following the MA treatment, the antifungal property was remarkably enhanced and met the Japanese Industrial Standard K1571. Therefore, MA treatment in the vapor phase is an effective method to attain antifungal properties as well as high dimensional stability with a small amount of nontoxic reagent.

Key words Dimensional stability · Durability · Maleic anhydride · Vapor phase reaction

Introduction

Various chemical modifications have been developed to enhance and improve the properties of wood, including dimensional stability, resistance to fungal attack, and me-

chanical properties. Recently, the safety of products relative to their surroundings, as well as a reduction of energy consumption from manufacturing to scrapping, are being increasingly emphasized. Taking such requirements into account, we have applied dicarboxylic and tricarboxylic acids to the chemical modification of wood. These carboxylic acids are promising in terms of satisfying the above-mentioned demands.

To date, Itoh et al.¹ have achieved high dimensional stability and antifungal activity by treatment with carboxyethylthiosuccinic acid. In addition, potassium persulfate-catalyzed treatment with aqueous maleic acid achieved an antishwelling efficiency (ASE) of about 60% with a weight increase (WPG) of only 3%.² Given the high ASE and small WPG, the formation of cross-links was assumed.

Fujimoto^{3,4} has reported that the dimensional stability and durability of wood were improved by treatment with a mixture of maleic acid and glycerol. The reaction is assumed to be mainly cross-link formation between carboxyl and hydroxyl groups.⁵ Roussel et al.⁶ reported that the dimensional stability, mechanical properties, and durability of wood increased by reaction with the adduct of maleic anhydride (MA) and polyglycerol.

Matsuda and Ueda⁷ developed an oligoesterified wood via an additional reaction between wood meal and MA or succinic anhydride, followed by the addition of dicarboxylic acid anhydride and epoxides. Although oligoesterified wood can now be prepared in one step,⁸ it was generally known that the wood could be easily esterified with MA according to the reaction shown in Fig. 1.^{9,10}

For example, an ASE of about 50% was attained with a WPG of 25% as a result of the reaction of wood with MA.¹¹ However, several issues, i.e., poor dimensional stability, difficulty in the recovery of reagent, and employment of organic solvent for the leaching of unreacted reagent, were unsolved.

In order to achieve a high ASE with less reagent and greater permanence, we examined the optimum reaction conditions for wood and vaporous MA. After examining the effects of the reagent, initial moisture content, and reac-

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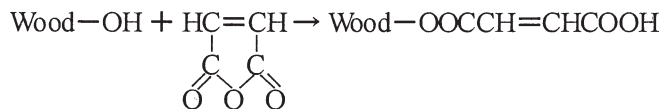


Fig. 1. Esterification of wood with maleic anhydride

tion temperature, we discuss the mechanism of dimensional stabilization. The antifungal properties of MA treatment were also evaluated.

Materials and methods

Wood samples and reagent

Sugi (*Cryptomeria japonica* D. Don) sapwood specimens 28 (T) \times 28 (R) \times 5 mm (L) were used for the evaluation of dimensional stability. Six matched specimens were assigned for each reaction condition. For the fungal decay tests, 24 pieces of sugi sapwood, 20 (T) \times 20 (R) \times 10 mm (L), were used for each reaction condition.

The specimens were oven-dried at 105°C for 24 h before being weighed and measured. The specimens for the evaluation of dimensional stability were then conditioned over saturated salt solutions in desiccators.

Reagent grade MA (Wako, Osaka) was used.

Vapor phase reaction with MA

Conditioned specimens were placed in a preheated (90°C) glass vessel (6.7 l) along with a defined amount of MA, and then the whole vessel was evacuated, tightly stoppered, and heated in an oven at 90°C. After 12 h, the temperature was elevated to 150°C or 180°C for 12 to 24 h. The initial moisture content of the specimens was 0%, 4.6%, 11.0%, and 19.1%, and the internal pressure of the vessel was about 7 hPa, when it was evacuated without contents. After the reaction, the vessel was opened and allowed to cool for about 1.5 h. Then the specimens were heated in an oven at 105°C for 120 h to remove unreacted MA.

The WPG was calculated from the oven-dried weight before and after treatment, and the bulking coefficient (B) was defined as follows,

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

where a_0 and a_1 are the oven-dried cross-sectional area before and after treatment, respectively.

The MA supplied to the wood specimens (total oven-dry weight: ca. 9.2 g) was varied from 1.47 to 14.7 g (MA/wood = 16/100 to 160/100 by weight). The concentration of MA in the vapor phase was about $2.2\text{--}22 \times 10^{-3} \text{ mol l}^{-1}$ assuming the MA vaporizes completely and behaves as an ideal gas.

The specimens for fungal decay tests were prepared using 12 pieces at one time, and the reaction was repeated

twice. To the specimens (total oven-dry weight: ca. 17 g), 2.61 or 5.23 g of MA was added (MA/wood = 15/100 or 30/100). The initial moisture content of the specimens was about 10%. The concentration of MA in the vapor phase was about 4.0 or $8.0 \times 10^{-3} \text{ mol l}^{-1}$ under the assumption stated above. Control specimens were heated in the absence of MA in a similar manner.

Dimensional stability tests

The antismelling efficiency in a water-saturated state (ASE_w) was defined by,

$$\text{ASE}_w(\%) = \frac{S_w^u - S_w^t}{S_w^u} \times 100 \quad (2)$$

where S_w^u and S_w^t are the coefficients of swelling for untreated and treated wood, respectively, which were evaluated from the cross-sectional area in oven-dried and water-saturated states.

The reduction in water absorption (RWA_R), which evaluates the decrease in water absorptivity of wood substance, was defined by,

$$\text{RWA}_R(\%) = \frac{W^u - W_R^t}{W^u} \times 100 \quad (3)$$

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 weight (w_1) and water-saturated weight (w_2) after treatment as follows,

$$W_R^t(\%) = \frac{w_2 - w_1}{w_0} \times 100 \quad (4)$$

The specimens were then oven-dried again, and conditioned at 20°C and 92% relative humidity (RH) for about 1 month. The antismelling efficiency in the conditioned state (ASE_m) was calculated in a similar manner to ASE_w from the coefficient of cross-sectional swelling at 20°C and 92% RH on the basis of the oven-dried state. Especially for treated specimens, the coefficient of swelling (S_m^t) was calculated from the oven-dried cross-sectional area after once saturated in water (a_3) and the conditioned (20°C and 92% RH) cross-sectional area (a_4) as follows,

$$S_m^t(\%) = \frac{a_4 - a_3}{a_3} \times 100 \quad (5)$$

Moreover, a reduced moisture-excluding efficiency (MEE_R) was defined by,

$$\text{MEE}_R(\%) = \frac{M^u - M_R^t}{M^u} \times 100 \quad (6)$$

where M^u is the moisture content of the untreated specimen, and M_R^t is a reduced moisture content, i.e., moisture content of treated specimens defined by,

$$M_R^t(\%) = \frac{w_4 - w_3}{w_0} \times 100 \quad (7)$$

where w_3 is the oven-dry weight of the treated specimen, and w_4 is the weight at 20°C and 92% RH of the treated specimen.

The water soaking (attained by keeping at 40hPa for 2h, at 1.37MPa for 2h, and at ambient pressure while dipping in water for 24h) and oven drying (50°C then 105°C for each 24h) were repeated three more times; then the specimens were again conditioned at 20°C and 92% RH.

Fungal decay tests

The specimens were subjected to fungal decay tests according to JIS K1571: 1998.¹² We defined the retained WPG as well as the weight loss (WL) provided in JIS. The oven-dried state was achieved at 105°C but not at 60°C. The retained WPG and the WL were defined as follows,

$$\text{Retained WPG}(\%) = \frac{w_5 - w_0}{w_1 - w_0} \times 100 \quad (8)$$

$$\text{WL}(\%) = \frac{w_5 - w_6}{w_5} \times 100 \quad (9)$$

where w_5 is the oven-dry weight of the treated specimen after weathering, w_6 is the oven-dry weight after the decay test, and w_0 and w_1 are the same as defined earlier.

Results and discussion

Effect of MA/wood ratio on dimensional stability and related properties

In Table 1, the WPG, take up of MA, B , and ASE_w are summarized against the weight ratio of supplied MA to wood. In these cases, the reactions were carried out by consecutive heating at 90°C for 12h and 150°C for 12h of specimens with an initial moisture content (MC) of about 8%.

The WPG increased with the ratio of supplied MA, and about 50% of MA was taken up into wood irrespective of the amount supplied. When the supply was low (MA/wood = 16/100 or 32/100), a moderate ASE_w (40%–50%) was attained with a small B (2%–4%).

Table 1. Dependence of weight increase (WPG), bulking coefficient (B), and antiswelling efficiency (ASE_w) on the weight ratio of maleic anhydride (MA) to wood

MA/wood ^a	Vapor phase MA concentration (mol ⁻¹) ^b	WPG (%)	Take-up (%)	B (%)	ASE_w (%)
16/100	2.2×10^{-3}	8.2	51	2.19	40.2
32/100	4.5×10^{-3}	18.6	60	3.84	50.5
160/100	22×10^{-3}	69.7	44	13.03	48.5

Initial moisture content (MC): ca. 8%. Reaction conditions: 90°C 12h + 150°C 12h

^aThe weight ratio of MA to total oven-dry weight of six untreated specimens

^bConcentration of MA in the vapor phase was estimated under the assumption that MA vaporizes completely and behaves as an ideal gas

In Fig. 2, the total amount of swelling is plotted against MA/wood ratio. The total amount of swelling includes the expansion due to the introduction of reagent (i.e., the bulking coefficient B) and that due to water absorption itself, and is calculated from the cross-sectional area in the oven-dried state before treatment (a_0) and that in water-saturated state after treatment (a_2) as follows:

$$\text{Total amount of swelling}(\%) = \frac{a_2 - a_0}{a_0} \times 100 \quad (10)$$

Figure 2 shows that when the supply of MA was low, the total swelling of the treated specimens was smaller than the coefficient of swelling of untreated samples (S_w^u). These results resemble those of formaldehyde treatment where dimensional stability is mainly achieved by the formation of cross-links.

When the reaction was carried out with a high MA/wood ratio (160/100), microchecks appeared on the surface of the specimens. Furthermore, although the B of treated specimens was as much as the S_w^u , the ASE_w was the same as in the case of a low MA supply (MA/wood = 16/100).

Figure 3 illustrates the changes in WPG with repeated wetting and drying, and the changes in moisture content accompanying the decrease in WPG. When the reaction was carried out with a higher MA/wood ratio, the WPG decreased more remarkably. After leaching, M_R^t became as low as M^u . These results suggest that unreacted reagent remaining in the wood specimen caused the high M_R^t , other-

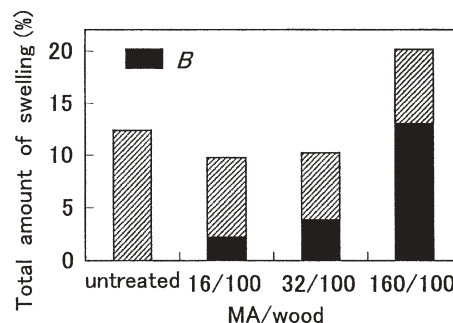


Fig. 2. Total amount of swelling for the untreated and treated specimens. Moisture content (MC): ca. 8%; reaction conditions: 90°C 12h + 150°C 12h. Total amount of swelling = $[(a_2 - a_0)/a_0] \times 100$, where a_0 = oven-dried cross-sectional area before treatment, a_2 = cross-sectional area in water-saturated state after treatment. B , Bulking coefficient

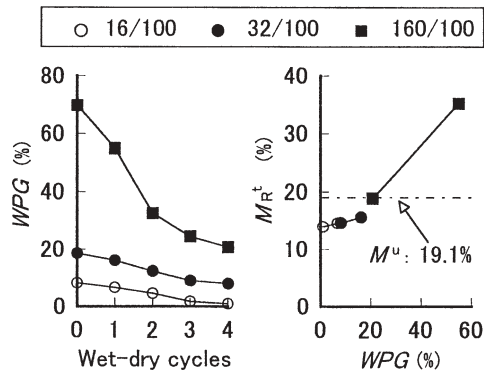


Fig. 3. The changes of weight increase (WPG) with repeated wetting and drying, and relationship between WPG and reduced moisture content (M_R^t) at 20°C and 92% relative humidity (RH) for different MA/wood ratios. MC: ca. 8%; reaction conditions: 90°C 12h + 150°C 12h. M^u , Moisture content of untreated specimens

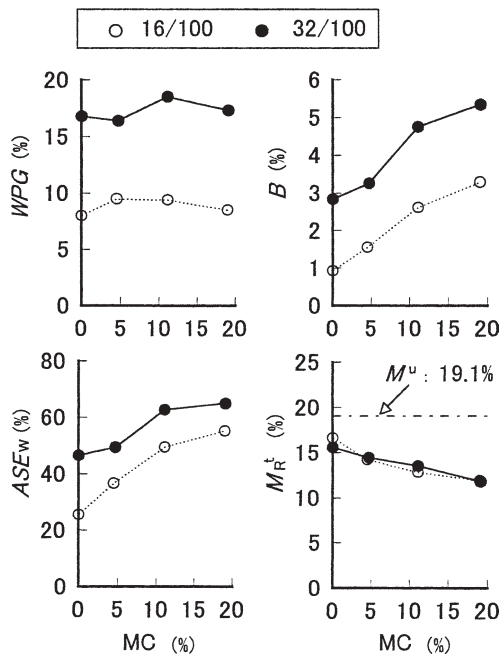


Fig. 4. Effect of MC on WPG, B , antiswelling efficiency (ASE_w), and M_R^t . Reaction conditions: 90°C 12h + 150°C 12h

wise once formed monoester hydrolyzed to maleic acid, which may result in moisture adsorption. On the other hand, when the supply of MA was low, the M_R^t values of treated specimens were lower than M^u , regardless of the wet and dry treatment.

Effect of initial moisture content on dimensional stability and related properties

Figure 4 shows the effect of initial moisture content (MC) on ASE_w , WPG, and so on. The reaction was carried out with a weight ratio of MA to wood of 16/100 or 32/100, and consecutive heating at 90°C for 12h and 150°C for 12h.

The WPG depended little on MC, whereas B and ASE_w increased and M_R^t decreased with increasing MC. The pen-

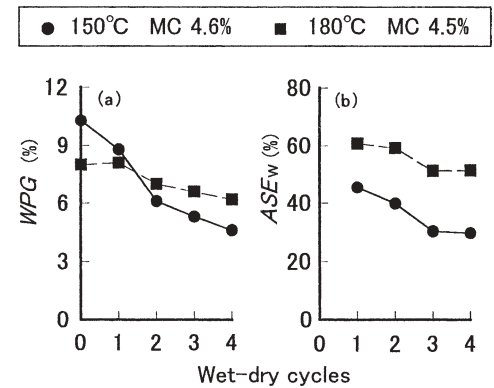


Fig. 5. The changes of WPG (a) and ASE_w (b) with repeated wetting and drying. MA/wood: 16/100; reaction conditions: 90°C 12h + each reaction temperature for 24h

etration of MA into the cell wall may become easier with the swelling of the cell wall, or perhaps bulky maleic acid, which results from the reaction between MA and water, may penetrate into the cell wall. In any case, it is a fact that the dimension-stabilizing effect increased in the presence of water molecules, although the role of water could not be clarified.

Effect of reaction temperature on dimensional stability and related properties

A series of reactions was carried out with a MC of 4.5%, a MA/wood weight ratio of 16/100, preheated at 90°C for 12h, and heated for 24h at each variable temperature. When the second heating stage was carried out at 180°C, about 75% of WPG was retained even after four wet-dry cycles (Fig. 5a). This suggests that the reagent was effectively fixed with rising temperature, and that the higher the reaction temperature is, the higher are the initial ASE_w values and its endurance (Fig. 5b).

After one wet-dry treatment and successive conditioning at 20°C and 92% RH, the M^u was 19.2%, and the M_R^t values were 13.5% and 9.8% for the specimens treated at 150° and 180°C, respectively. For the specimens heated under vacuum at 150° and 180°C without MA, the M_R^t values were 16.9% and 14.1%, respectively. From these results, the decrease of hygroscopicity of MA-treated wood may be attributed to esterification as well as thermal effects. Evidence of esterification was also observed by means of diffuse reflectance infrared Fourier transform spectroscopy, and will be referred to in the following report.

Mechanism of dimensional stabilization

Figure 6 shows the relationships between WPG and B and between B and ASE_w during the four wet-dry cycles for the specimens treated with a MA/wood weight ratio of 16/100, a MC of 0%–11%, preheated at 90°C for 12h, and heated at 150° or 180°C for 24h. As shown in Fig. 6a, B increased in proportion to WPG and the slopes did not differ among reaction conditions. This suggests that the expansion caused

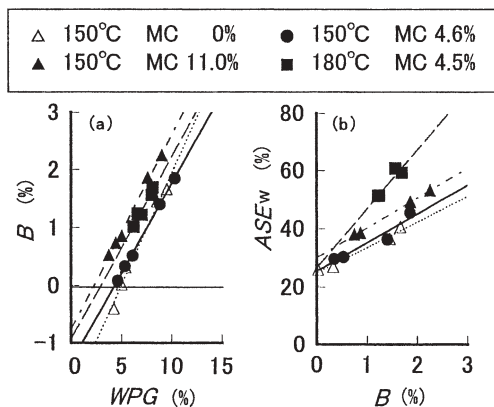


Fig. 6. Relationship between **a** WPG and B , and between **b** B and ASE_w . MA/wood: 16/100; reaction conditions: 90°C 12h + each reaction temperature for 24h

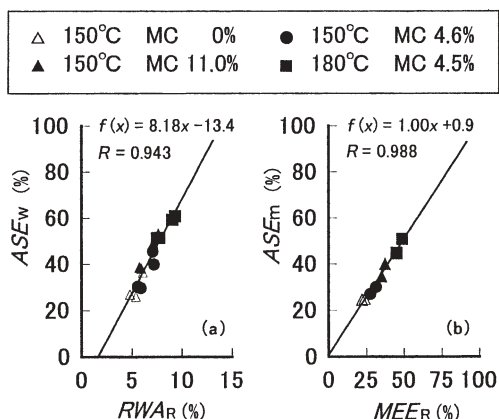


Fig. 7. Relationship between **a** reduction in water absorption (RWA_R) and ASE_w , and between **b** reduced moisture-excluding efficiency from oven-dried condition to 20°C and 92% RH (MEE_R) and antiswelling efficiency from oven-dried condition to 20°C and 92% RH (ASE_m). MA/wood: 16/100; reaction conditions: 90°C 12h + each reaction temperature for 24h

by the introduction of one MA molecule in the cell wall is independent of the reaction conditions. It also came to light that WPG at $B = 0$, namely the MA that does not contribute to B , tends to decrease with increasing MC and reaction temperature. In the regression lines of Fig. 6b, the intercepts of the ordinate were positive, which suggests the existence of a dimension-stabilizing mechanism other than the bulking effect. This was also proposed by Itoh and Ishihara¹³ for treatment with 4,5-dihydroxy-1,3-bis(hydroxymethyl)imidazolidin-2-one. The increase in the slope of the regression line accompanying the rise in temperature shows the enhancement of the dimension-stabilizing efficiency of the MA molecule in the cell wall.

The dimension stabilization is generally attributable to the decrease of hygroscopicity and/or bulking of introduced reagent. Figure 7 shows good correlations for RWA_R vs ASE_w and MEE_R vs ASE_m during four wet-dry cycles, which suggests the dimensional stabilization by MA treatment arises predominantly from decreased hygroscopicity.

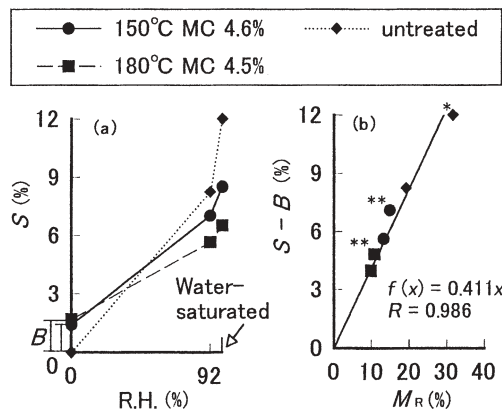


Fig. 8. Swelling behavior for the untreated and treated specimens. MA/wood: 16/100; reaction conditions: 90°C 12h + each reaction temperature for 24h. S , Coefficient of cross-sectional swelling, which was calculated on the basis of the oven-dried cross-sectional area before treatment; asterisk, $M_R = W^u - 198$ (%); two asterisks, $M_R = W_R^1 - 198$ (%)

Figure 8a shows the swelling behavior of the treated specimens after a single treatment of water saturation and oven drying, as well as that of an untreated specimen. The coefficient of cross-sectional swelling (S) was always calculated on the basis of the oven-dried cross-sectional area (a_0) before treatment. The S values for treated specimens (water saturated and conditioned at 20°C and 92% RH) were smaller than those of untreated specimens, and the differences became larger with rising temperature. Moreover, the change of S from conditioned to the water-saturated state was smaller for the treated specimens than for the untreated one. This shows that the swelling of treated wood was restrained at high humidity (92% RH to the water-saturated state), and suggests the formation of cross-links.

Figure 8b shows the relationship between M_R and $S - B$, where B is the bulking coefficient after one water soaking, and is the S value at RH = 0% in Fig. 8a. In this figure, M_R^1 or M^u is totally expressed by M_R , and that in the water-saturated state was estimated as follows. In order to estimate the moisture content of the cell wall, it is necessary to subtract the free water in the cell lumen. The amount of free water was obtained by extrapolation of the regression line in Fig. 7a to $ASE_w = 100\%$, where water should not exist in the cell wall. The RWA_R (13.9%) estimated from Fig. 7a corresponds to a moisture content of 198%, because W^u was 230%. The values for M_R in the saturated state obtained by subtracting 198% from W^u or W_R^1 were 32%, 15%, and 11% for untreated wood, and for wood treated at 150° and 180°C, respectively. From the good correlation in Fig. 8b, it was certified that the swelling is restrained by lowering of the moisture content of the cell wall.

Antifungal property

The results of the fungal decay test are summarized in Table 2. The retained WPG after the weathering test was markedly high in all MA treatments tested. Moreover, the WL values of treated specimens were remarkably low. For

Table 2. The results of the fungal decay test based on JIS K 1571: 1998

Reaction temperature (°C)	MA/wood	Vapor phase MA concentration (mol l ⁻¹)	WPG (%)	Retained WPG (%) ^a	WL (%) ^b	
					<i>Fomitopsis palustris</i>	<i>Trametes versicolor</i>
150	0/100	0	-0.8	-	55.5 (10.1)	36.5 (4.2)
150	30/100	8.0 × 10 ⁻³	16.1	76.1	5.2 (1.8)	2.5 (0.3)
180	0/100	0	-2.0	-	51.2 (5.1)	29.2 (5.5)
180	15/100	4.0 × 10 ⁻³	5.5	79.6	4.4 (2.9)	1.8 (0.5)
180	30/100	8.0 × 10 ⁻³	14.0	93.5	1.0 (0.2)	1.2 (0.3)
Untreated					52.4 (7.1)	44.0 (8.6)

Values in parentheses are standard deviations. MC: ca. 10%. Reaction conditions: 90°C 12h + each reaction temperature 24h

^a Retained WPG (%) = $[(w_5 - w_0)/(w_1 - w_0)] \times 100$, where w_0 = oven-dried weight before treatment, w_1 = oven-dried weight after treatment, w_5 = oven-dried weight of treated specimen, after weathering test according to JIS K 1571: 1998

^b WL (%) = $[(w_5 - w_6)/w_5] \times 100$, where w_5 is as above, w_6 = oven-dried weight after decay test

example, when the specimen was treated at 180°C (WPG = 14.0%), the WL values were as low as 1.0% and 1.2% against attack by *Fomitopsis palustris* and *Trametes versicolor*, respectively. According to JIS K1571: 1998,¹² the prescribed upper limit of WL for a wood preservative is 3%. MA treatment met this criterion, although MA is not a preservative substance. Therefore, treatment using MA in the vapor phase is an effective method to attain antifungal properties as well as dimensional stability.

Conclusions

The chemical modification of wood with MA was carried out in a vapor phase reaction system. The reagent supplied to the reaction system was effectively absorbed by the wood, and the take-up of MA reached around 50%. Even at a low MA/wood weight ratio, satisfactorily high dimensional stability was achieved. The water molecules present in the cell wall advanced the dimension-stabilizing efficiency. When the reaction was conducted at 180°C, the leaching of reagent during the water soakings and the swelling at high humidity were decreased, and a high ASE was attained with a small *B* value. These results suggest the formation of cross-links in the cell wall. The antifungal property was remarkably improved and met the standard of JIS K1571: 1998.¹²

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