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## Influences of moisture content on the catalysis of sulfur dioxide and attainable properties in a vapor-phase treatment of wood with formaldehyde

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**Abstract** Influences of moisture content on the catalysis of sulfur dioxide and physical properties of reaction products were examined for a vapor-phase treatment of spruce wood with formaldehyde. The reaction rate was strongly dependent on the amounts of water and sulfur dioxide in the reaction system, and this was consistent with a proposal that the hydroxymethylsulfonic acid ( $\text{HOCH}_2\text{SO}_3\text{H}$ ) formed from sulfur dioxide, water, and formaldehyde acts as a catalyst for the reaction. However, not all water molecules contributed to the formation of  $\text{HOCH}_2\text{SO}_3\text{H}$ , because some were adsorbed by the wood components. When the initial moisture content was high, polymeric cross-linking was likely because the ultimate weight gain was much greater than the value estimated based on monomeric cross-links. The lower values of antiswelling efficiency and higher equilibrium moisture content at a specific level of weight gain also suggested the existence of polymeric cross-links. However, the difference in the length of cross-links did not significantly influence the mechanical properties.

**Key words** Formaldehyde treatment · Reaction kinetics · Sulfur dioxide · Dimensional stability · Physical property

### Introduction

Formaldehyde treatment is one of the most well-known methods for the chemical modification of wood as well as

cellulosic materials, but the product is far removed from the wood put to practical use. Nevertheless, it has often been subjected to physical and mechanical studies as a typical reaction where cross-links are formed between hydroxyl groups in wood components.<sup>1</sup> In such cases, mechanical properties have been correlated with the extent of the reaction; weight gain and dimensional stability are usually adopted as measures of the progress of the reaction. However, the properties of the wood would be dependent not only on the extent of the reaction but on the mechanism of it.

According to Guthrie,<sup>2</sup> polymeric cross-links are formed when the reaction is carried out in a swollen state. Joarder et al.<sup>3</sup> reported that the distribution of cross-links in the cell wall differs between uncatalyzed and catalyzed reactions. They showed that cross-links are distributed uniformly in the uncatalyzed reaction, while they concentrate at the periphery of the cell wall in the catalyzed one. If the length or distribution of cross-links differ depending on the reaction conditions, it is likely that the physical properties are not the same at a definite reaction level. In fact, Minato<sup>4</sup> reported that the mechanical strength of paper cross-linked with formaldehyde is superior under noncatalytic rather than catalytic conditions.

In this study, we intended to clarify the catalytic role of  $\text{SO}_2$  in relation to the amount of water molecules in the reaction system. The formaldehyde treatment was carried out in the vapor phase with excess formaldehyde and various combinations of moisture contents and  $\text{SO}_2$  concentrations. Moreover, we examined whether the property of the reaction product differs depending on the reaction conditions.

Studies on the physical and mechanical properties of wood are making steady progress, accompanying advances in analytical technology. The results of this study will lead to better wood samples for studies in these fields.

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**Table 1.** Saturated salt solutions used for the conditioning, expected relative humidity, and achieved moisture content at 20°C

Salt	Relative humidity (%)	Moisture content (%)	
		Cross section	Strip
LiCl	11	4.34	4.02
MgCl <sub>2</sub>	33	5.30	6.72
Mg(NO <sub>3</sub> ) <sub>2</sub>	54	9.05	10.6
NaCl	75	12.5	13.1
CaCl <sub>2</sub>	85	15.8	–

## Experiment

### Specimens

Sitka spruce (*Picea sitchensis* Carr.) was cut to specimens measuring 30 (T) × 30 (R) × 5 mm (L) or 2 (T) × 12 (R) × 160 mm (L). The former specimens were used for the evaluation of weight gain, dimensional stability, and so on, after extraction with an ethanol and benzene solution (v/v = 1:2) for 8 h. The latter specimens were subjected to a vibrational property test without extraction. Before formaldehyde treatment, both specimens were conditioned over saturated solutions of various salts at 20°C for more than 2 weeks. Table 1 shows the kind of salts used, relative humidity expected at 20°C, and equilibrium moisture content observed.

### Formaldehyde treatment

The treatment was carried out in a 4-l airtight glass vessel. Three conditioned pieces of wood sample and 3 g of reagent-grade paraformaldehyde (Merck) were placed in the preheated (120°C) vessel. The vessel was evacuated once and SO<sub>2</sub> was volumetrically introduced by means of a large glass syringe through a joint and stopcock attached to the vessel. The vessel was then heated in an oven at 120°C for 1–24 h.

Because the moisture content of sample should change during these procedures, the moisture content just before the treatment was referred to as the initial moisture content. The subsequent moisture content became a variable of the reaction conditions. When paraformaldehyde vaporizes completely and the vapor behaves as an ideal gas, the concentration of formaldehyde in the vapor phase would be 25 mmol/l. The concentration of SO<sub>2</sub> ranged from 0.56 to 4.46 mmol/l.

After treatment, the samples were sufficiently rinsed with running water for more than 2 days and the dimensions in water-saturated state were measured. They were then dried at 105°C for 2 h and subjected to the measurement of the weight and dimensions.

### Definitions

Weight gain (WG), antiswelling efficiency (ASE), bulking, and equilibrium moisture content (EMC) were defined as follows;

$$WG(\%) = \frac{w_t - w_0}{w_0} \times 100 \quad (1)$$

$$ASE(\%) = \frac{s_t - s_0}{s_0} \times 100 \quad (2)$$

$$Bulking(\%) = \frac{v_t - v_0}{v_0} \times 100 \quad (3)$$

$$EMC(\%) = \frac{w_c - w_t}{w_t} \times 100 \quad (4)$$

where,  $w_0$  and  $w_t$  are oven-dry weights before and after treatment,  $s_0$  and  $s_t$  are swelling coefficients of untreated and treated specimens,  $v_0$  and  $v_t$  are oven-dry volumes before and after treatment, respectively, and  $w_c$  is the weight of a treated specimen conditioned in a chamber kept at 20°C and 60% relative humidity (RH).

### Measurement of vibrational properties

According to a free-free flexural method,<sup>5</sup> the specific dynamic Young's modulus ( $E/\gamma$ ) and loss tangent ( $\tan \delta$ ) were determined after conditioning at 20°C and 65% RH for more than 2 weeks. From the  $E/\gamma$  and  $\tan \delta$  before and after treatment, percent changes were calculated as follows:

$$\text{Change of } E/\gamma(\%) = \frac{(E/\gamma)_t - (E/\gamma)_0}{(E/\gamma)_0} \times 100 \quad (5)$$

$$\text{Change of } \tan \delta(\%) = \frac{(\tan \delta)_t - (\tan \delta)_0}{(\tan \delta)_0} \times 100 \quad (6)$$

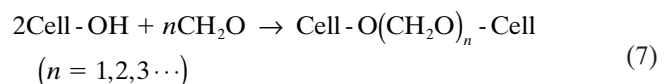
where, subscripts 0 and t represent before and after treatment, respectively.

## Results and discussion

### Dependence of initial moisture content and concentration of SO<sub>2</sub> on reaction rate

Figure 1 shows the profiles of WG with the passage of reaction time, where the initial moisture content ranged from oven dry to 15.8%, while the concentration of SO<sub>2</sub> was fixed at 2.23 mmol/l. The WG increased more steeply with the rise of initial moisture content, and exceeded 7% within this experiment.

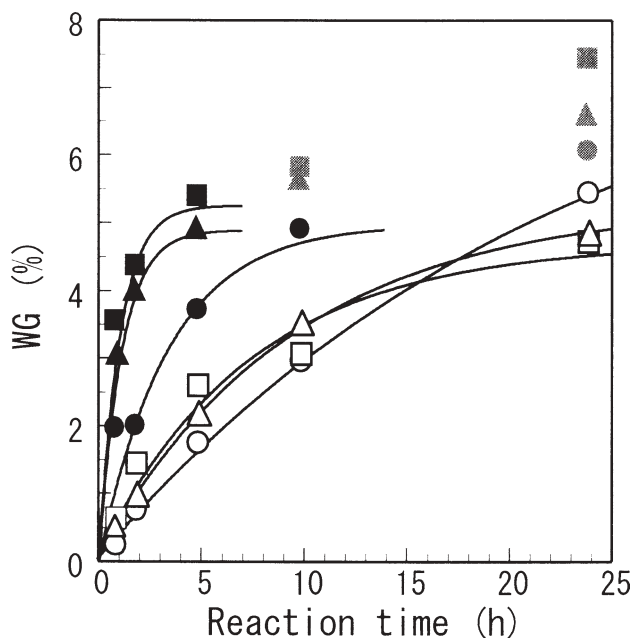
The reaction between cellulose and formaldehyde has been proposed as follows,<sup>2</sup>



where, Cell-OH represents the hydroxyl group in cellulose or wood constituents and  $n$  is the length of the cross-link. Concerning the extent of the reaction between cellulosic materials and formaldehyde, about 2% to 3% for cotton

**Table 2.** Reaction parameters and correlation coefficients

Initial moisture content (%)	[SO <sub>2</sub> ] (mmol/l)	Data used for regression	<i>a</i> (%)	<i>k</i> (h <sup>-1</sup> )	<i>r</i> <sup>2</sup>
0.0	2.23	0–24 h	8.30	0.0437	0.999
4.34	2.23	0–24 h	5.26	0.104	0.999
5.30	2.23	0–24 h	4.68	0.1354	0.975
9.05	2.23	0–10 h	4.98	0.2961	0.964
12.5	2.23	0–5 h	4.90	0.9195	0.998
15.8	2.23	0–5 h	5.27	0.9849	0.994
5.58	0.56	0–24 h	7.02	0.0466	0.989
5.58	1.12	0–24 h	4.70	0.1192	0.989
5.58	2.23	0–24 h	4.68	0.1354	0.975
5.58	4.46	0–24 h	5.10	0.1174	0.995



**Fig. 1.** Profile of weight gain (WG) with the passage of reaction time (classified by initial moisture content). Concentration of SO<sub>2</sub>: 2.23 mmol/l, initial moisture content: open circles, 0%; open triangles, 4.34%; open squares, 5.30%; filled circles, 9.05%; filled triangles, 12.5%; filled squares, 15.8%. Gray symbols were not used for the regression

cellulose and 4% to 5% for wood are generally reported, however, few reports refer to the ultimate extent of the reaction. When we made estimates, the ultimate value under the assumption that the cross-links were monomeric, i.e.,  $n = 1$ , it was 5.50% or 5.28% depending on the estimation of the number of accessible hydroxyl groups by Norimoto<sup>6</sup> or Hill and Jones,<sup>7</sup> respectively. Actually, WG was much higher than the calculated value when the initial moisture content was higher than 9.05%. This suggests the existence of polymeric cross-links by oxymethylene chain.

The reaction rate between hydroxyl groups in wood components and formaldehyde may be proportional to the product of the formaldehyde concentration, [CH<sub>2</sub>O], and the residual amount of accessible hydroxyl groups in the substrate, [OH], as follows;

$$\text{Reaction rate} = -d[\text{OH}]/dt = k'[\text{CH}_2\text{O}] \cdot [\text{OH}] \doteq k[\text{OH}] \quad (8)$$

If the amount of formaldehyde exceeds that of accessible hydroxyl groups,  $k'[\text{CH}_2\text{O}]$  can be substituted for  $k$  and the reaction can be approximated using a pseudo first-order rate equation.

In our experimental procedure, formaldehyde cannot exist in excess throughout the course of the reaction, because the vaporization of paraformaldehyde may be insufficient in the early stage of the reaction. Nevertheless, because a delay in the increase of WG, namely an induction period of the reaction, was not observed in the initial stage of the reaction, regression by the integration of Eq. 8,

$$x = a(1 - e^{-kt}) \quad (9)$$

was tried.  $x$  (%) is WG at reaction time  $t$  (h), and  $a$  (%) is the ultimate value of WG.

When the regression equation was applied to whole data, the regression curve tended to deviate from the observed values, notably in the case of a high initial moisture content. This is a typical characteristic of a heterogeneous reaction, often found when the reaction is carried out at an elevated temperature and/or with a high catalyst concentration. In such cases, the diffusion of the reagent to the reaction site cannot follow a rapid reaction, and examples have also been observed for acetylation.<sup>8</sup> Moreover, polymeric cross-links are probable at extremely high WG. Therefore, the regression was conducted excluding the data greater than 5.5% of WG which is a theoretical value based on the proposal by Norimoto.<sup>6</sup> The time range of the data used for the regression is listed along with the rate constant, ultimate WG, and ratio of contribution ( $r^2$ ) in Table 2, and the regression curves are shown in Fig. 1.

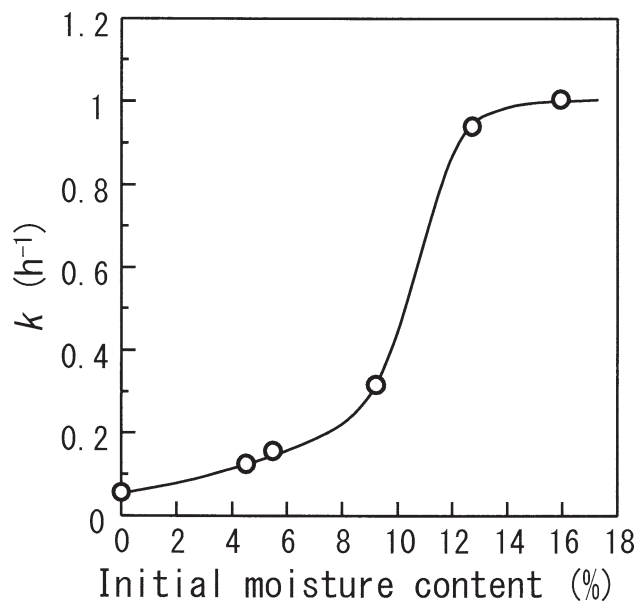
Figure 2 shows the dependence of  $k$  on the initial moisture content. The  $k$  value increased suddenly when the initial moisture content rose above 9.05%. The reaction may be accelerated in two ways accounting for the water in the system: by the swelling of the cell wall, which advances the diffusion of reagent, or by promoter action.

It has been proposed that SO<sub>2</sub> forms hydroxymethylsulfonic acid as a result of a reaction with water and formaldehyde as follows,<sup>9</sup>



According to this formula, the hydroxymethylsulfonic acid generated from SO<sub>2</sub>, H<sub>2</sub>O, and formaldehyde functions as a catalyst. In this reaction series, the amount of SO<sub>2</sub> was fixed

to 8.92 mmol, whereas that of H<sub>2</sub>O brought into the reaction vessel was 12.8 to 47.2 mmol depending on the total sample weight and initial moisture content (Table 3). Therefore, the moles of H<sub>2</sub>O stoichiometrically exceeded those of SO<sub>2</sub> even when the initial moisture content was at its lowest, and the yield of hydroxymethylsulfonic acid should be controlled by SO<sub>2</sub>. Nevertheless, *k* increased with the rise in the initial moisture content. This suggests that not all the water molecules in the reaction system contribute to the production of hydroxymethylsulfonic acid, with some molecules adsorbed by the wood. The sudden increase in *k* observed in Fig. 2 is attributable to the increase in water molecules involved in multilayer adsorption, whose bonding force is weaker than that in the monolayer. The pattern of increase in *k* reflects that of the water adsorbed by the multilayer.<sup>10</sup> The moisture content which forms a monolayer was estimated to be about 5%–6% for wood.<sup>11</sup> The water molecules absorbed by the multilayer swell the cell wall more so than those of the monolayer. The acceleration of the diffusion of reagent may be another reason why *k* increased at high moisture content. The leveling off of *k* as the



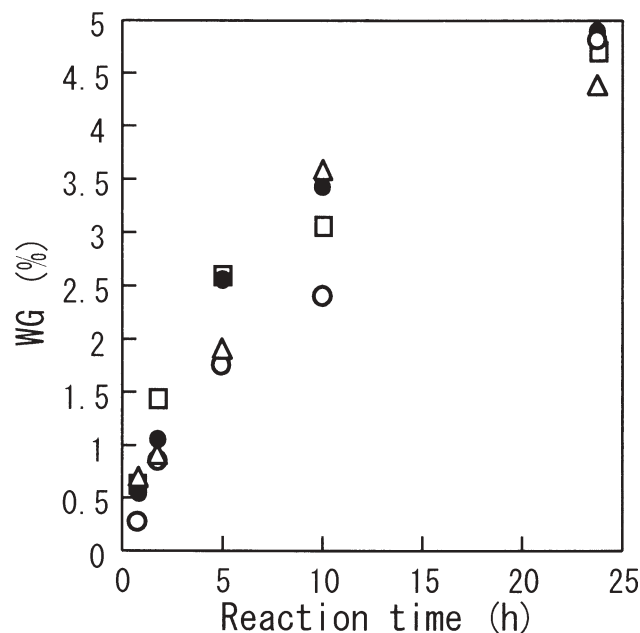
**Fig. 2.** Dependence of rate constant on the initial moisture content. Concentration of SO<sub>2</sub>: 2.23 mmol/l

initial moisture content rose above 12% suggests a lack of SO<sub>2</sub>.

Figure 3 shows the profiles of WG with the passage of reaction time, where the concentration of SO<sub>2</sub> varied from 0.56 to 4.46 mmol/l, while the initial moisture content was fixed at 5.58%. Also in these cases, the first-order rate equation was successfully applied (Table 2). The rate constant increased up to a catalyst concentration of 1.12 mmol/l, and then leveled off (Fig. 4).

In this series, the amount of water was 15.9 mmol, while that of SO<sub>2</sub> varied from 2.24 to 17.8 mmol (Table 3). Therefore, the yield of hydroxymethylsulfonic acid should increase with the increase in the number of moles of SO<sub>2</sub>. However, *k* increased little above 1.12 mmol/l of SO<sub>2</sub>. This result again shows that water molecules strongly adsorbed by wood components cannot contribute to the production of hydroxymethylsulfonic acid.

The result observed here supports the proposal that SO<sub>2</sub> does not act as a catalyst until hydroxymethylsulfonic acid is formed. An acidic catalyst accelerates not only the reaction



**Fig. 3.** Profile of weight gain (WG) with the passage of reaction time (classified by concentration of SO<sub>2</sub>). Initial moisture content: 5.58%, concentration of SO<sub>2</sub>: open circles, 0.56 mmol/l; triangles, 1.12 mmol/l; squares, 2.23 mmol/l; filled circles, 4.46 mmol/l

**Table 3.** Relationship between molar quantities of H<sub>2</sub>O and SO<sub>2</sub> in the reaction system for each reaction condition

Initial moisture content (%)	Amount of H <sub>2</sub> O (mmol) <sup>a</sup>	[SO <sub>2</sub> ] (mmol/l)	Amount of SO <sub>2</sub> (mmol)
4.34	12.8	2.23	8.92
5.30	15.2	2.23	8.92
9.05	27.2	2.23	8.92
12.5	37.8	2.23	8.92
15.8	47.2	2.23	8.92
5.58	15.9	0.56	2.24
5.58	15.9	1.12	4.48
5.58	15.9	2.23	8.92
5.58	15.9	4.46	17.8

<sup>a</sup> Calculated from the initial moisture content and total weight of specimens involved in the reaction vessel

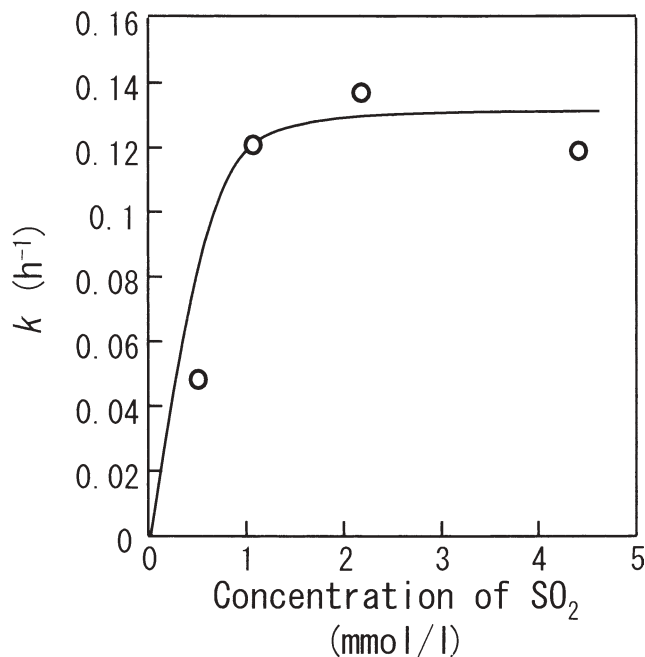


Fig. 4. Dependence of rate constant on the concentration of SO<sub>2</sub>. Initial moisture content: 5.58%

between wood components and formaldehyde, but also the degradation of wood itself. Thus an excessive amount of hydroxymethylsulfonic is not desirable. However, because the formation is controlled by the amount of water molecules added to the reaction system, the harmful influence of surplus SO<sub>2</sub> can be suppressed.

#### Dependence of initial moisture content on physical properties

In Fig. 5, the ASE estimated in the tangential and radial direction, bulking, and EMC are plotted against WG, where the initial moisture content ranged from oven dry to 15.8%, while the concentration of SO<sub>2</sub> was fixed at 2.23 mmol/l.

When the ASE was compared at a definite WG, it decreased slightly but obviously accompanying the increase in initial moisture content. At a higher moisture content, the intercellular space may expand and polymeric as well as monomeric cross-links will be formed between the hydroxyl groups in wood constituents. Therefore, fewer hydroxyl groups are involved in the cross-linking, and this results in a lower ASE even if the WG is the same.

The bulking was less extensive with a higher initial moisture content. This can also be related to the length of cross-links; however, we cannot find any plausible reason to explain the result.

The equilibrium moisture content at 20°C and 65% RH is also shown in Fig. 5. The higher the initial moisture content, the higher the EMC at a definite level of WG. This also reflects the existence of polymeric cross-links, which contribute less significantly to the decrease in EMC.

Figure 6 shows the changes of  $\tan \delta$  and  $E/\gamma$  resulting from the formaldehyde treatment, where the initial mois-

ture content ranged from 0% to 13.1%, while the concentration of SO<sub>2</sub> was kept at 2.23 mmol/l.

As mentioned above, the EMC at a specific WG level differed depending on the initial moisture content. Moreover, it has been reported that  $\tan \delta$  increases with moisture content in the normal humidity range.<sup>12</sup> Therefore, it is not strange even if the  $\tan \delta$  and  $E/\gamma$  would be affected differently depending on the initial moisture content. Nevertheless, the  $\tan \delta$  decreased and  $E/\gamma$  increased with increasing WG, while the tendencies did not distinctly differ among the reaction conditions.

For the mechanical properties, it will be necessary to investigate further.

## Conclusions

The dependence of the reaction rate for formaldehyde treatment on the reaction conditions was analyzed by applying a pseudo first-order rate equation. The reaction was accelerated with the rise of the initial moisture content, and leveled off above a specific SO<sub>2</sub> concentration. The results supported a mechanism of catalysis by SO<sub>2</sub>. Meanwhile, it was suggested that not all water molecules in the reaction system contribute to the formation of hydroxymethylsulfonic acid, with some molecules adsorbed by the wood components.

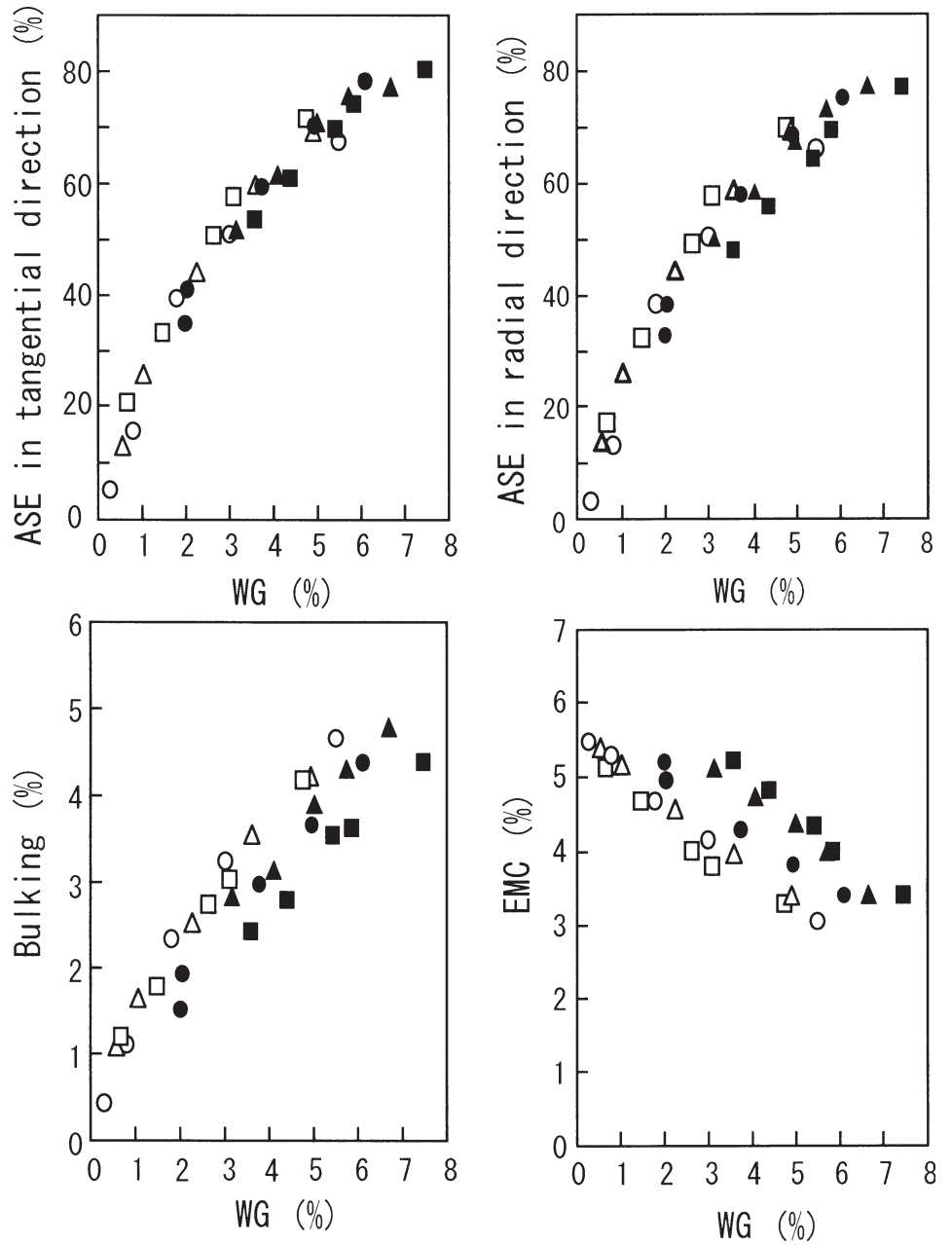
When the specimens were prepared with a high initial moisture content, the WG rose above the theoretical value. Furthermore, at a specific level of WG, the ASE was reduced and EMC was increased compared with those specimens prepared with a lower initial moisture content. These results implied the existence of polymeric cross-links.

The loss tangent and  $E/\gamma$  need to be examined with greater accuracy in order to exaggerate the effect of the reaction conditions.

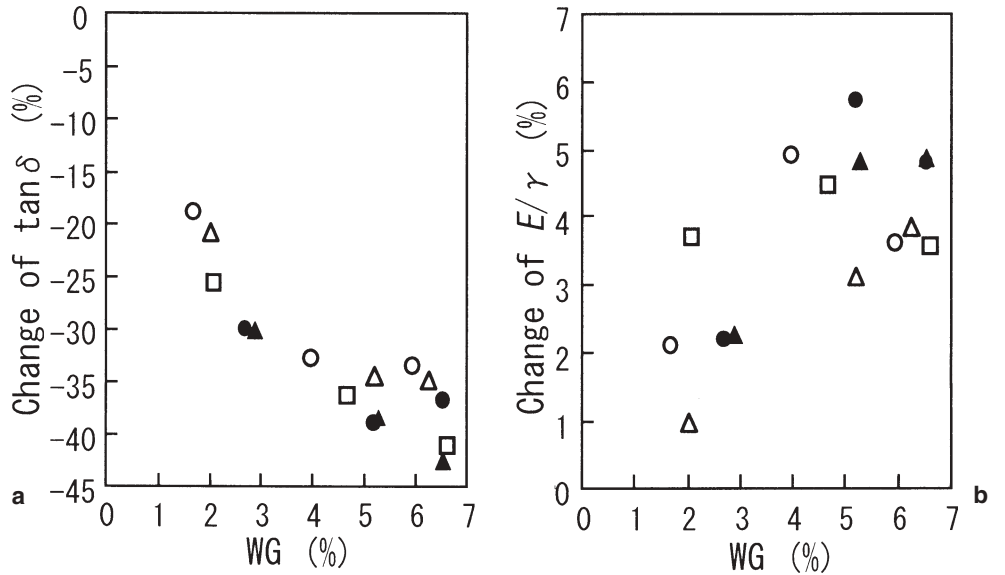
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**Fig. 5.** Variations in antishwelling efficiency (*ASE*) in tangential and radial directions, bulking, and EMC resulting from formaldehyde treatment with various WG. Symbols are the same as in Fig. 1. Concentration of  $\text{SO}_2$ : 2.23 mmol/l



**Fig. 6.** Changes of **a**  $\tan \delta$  and **b**  $E/\gamma$  resulting from formaldehyde treatment with various initial moisture contents. Concentration of  $\text{SO}_2$ : 2.23 mmol/l. Initial moisture content: open circles, 0%; open triangles, 4.02%; open squares, 6.72%; filled circles, 10.6%; filled triangles, 13.1%



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