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Na₂O-SiO₂ wood-inorganic composites prepared by the sol-gel process and their fire-resistant properties

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Abstract For enhancing fire-resistant properties, a binary system to prepare wood-inorganic composites was studied by adding sodium methoxide (SM) or sodium acetate (SA) to a reaction system for SiO₂ composites. Compared with the SiO₂ composites, both the Na₂O-SiO₂ composites prepared could be greatly improved up to 600°C–700°C (glowing). From scanning electron microscopic observations, this enhanced fire resistance was assumed to be due to chemical and physicochemical effects, such as dehydration and carbonization of wood by Na₂O gel. The glassy layer and intumescent structure formed over the cell walls were thought to prevent oxidation and heat transfer from proceeding into the inner portion of the wood cell walls. However, the reaction medium with SM to prepare Na₂O-SiO₂ composites was basic, whereas that with SA was rather neutral. In addition, in the latter composites, most of the inorganic gel was formed within the cell wall, retaining the porous structure characteristic of wood. Therefore, the Na₂O-SiO₂ composites prepared with SA can be concluded to be preferable for practical purposes.

Key words Wood-inorganic composites · Sol-gel process · Na₂O-SiO₂ · Thermal analysis · Fire resistance

Introduction

Although wood is an excellent natural composite, it has some unfavorable end-product properties regarding

dimensional stability, biodeterioration, and combustibility. Several attempts have been made to overcome such disadvantageous characteristics. The wood-inorganic material composites with barium phosphate or barium hydrogen phosphate prepared by the double diffusion process is a good example of enhancement of wood properties.¹ A similar trial was reported that prepared wood-inorganic composites from a colloidal silica solution system to form the inorganic deposits in wood.² Another trial was carried out particularly to enhance the fire resistance of wood reported that wood treated with boric acid and alkaline metal hydroxide has good fire resistance.³

In our laboratory, a sol-gel process has been applied to prepare wood-inorganic composites,^{4,15} and inorganic substances were found to be distributed differently in wood as various metal alkoxides were used with moisture-conditioned wood or water-saturated wood.^{4,5,8} Based on the results of a comparative study of the composites obtained, SiO₂ wood-inorganic composites prepared with moisture-conditioned wood are one of the most promising for property enhancement, with specifically deposited SiO₂ gels within the wood cell walls.

For enhancing the fire-resistant property of wood, we have applied trimethylphosphite (TMP) and/or trimethylborate (TMB) to the reaction system to prepare the SiO₂ wood-inorganic composites.^{9–11} The thermal properties of the obtained composites were evaluated, and these composites were found to have more enhanced fire-resistant properties than the SiO₂ composites. It was also found that various SiO₂ composites with fire-resistant agents could have attained enhanced fire-resistant properties.¹²

In this study, which is another attempt to enhance fire-resistant properties, we have applied sodium methoxide or sodium acetate to a reaction system for the SiO₂ wood-inorganic composites. The prepared Na₂O-SiO₂ wood-inorganic composites were then studied for their fire-resistant properties by thermal analysis, and the effects of the sodium compounds were evaluated regarding the fire resistance of the wood.

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Materials and methods

Wood specimens

The specimens [30 (R) × 30 (T) × 5 (L) mm] obtained from the sapwood portions of western hemlock (*Tsuga heterophylla* Sarg.) were extracted with acetone for 24 h and subsequently with water for another 24 h in a Soxhlet apparatus. Extracted wood specimens were then oven-dried, and their oven-dried weights were measured. To prepare the wood specimens with 20%–25% moisture content, oven-dried specimens were placed in a desiccator for 3 weeks at 20°C in which the relative humidity was controlled at 98% with a saturated salt solution of K₂SO₄.

Preparation of Na₂O-SiO₂ wood-inorganic composites

A solution was prepared with a molar ratio of 0.03:1.00:0.01 in methyltrimethoxysilane [(MTMOS), CH₃Si(OCH₃)₃], methanol, and acetic acid for preparing the SiO₂ wood-inorganic composites. To this solution, sodium methoxide (SM) (NaOCH₃) or sodium acetate (SA) (NaOCOCH₃) was added in molar ratios of 0.015, 0.030, and 0.060 to methanol to prepare the Na₂O-SiO₂ wood-inorganic composites with SM or SA.

Subsequently, the prepared solutions were impregnated into moisture-conditioned specimens at 20°C under a reduced pressure (15 mmHg) for 3 days. The impregnated specimens were then placed in an oven controlled at 60°C for 24 h and at 105°C for another 24 h to age the gels.

Evaluation of wood-inorganic composites

The pH of the reaction media for preparation of the Na₂O-SiO₂ wood-inorganic composites was measured with the pH meter (HORIBA D-13) at 20°C. The weight percent gain (WPG) of the composites was determined, on an oven-dried weight basis, by measuring the oven-dried weights of the extractive-free untreated specimens and the composite specimens. The bulking coefficient was also determined for the prepared composites.

For testing the thermal properties, about 8 mg of the composite specimens were studied with a thermogravi-

metric analyzer (Shimadzu TGA-50) and a differential thermal analyzer (Shimadzu DTA-50), with a flow of dried air at 50 ml/min. The temperature was raised from room temperature to 800°C at a rate of 20°C/min. These analyses were done one time for each specimen prepared.

For studying the distribution of the inorganic gels in the composites, the specimens were surfaced with a freeze microtome; the specimen were then mounted on a holder and carbon-coated. The exposed surfaces were studied with a JOEL scanning electron microscope (JEOL JSM-T330A) coupled with an EDAX 9100/70 energy-dispersive X-ray analyzer (SEM-EDXA) at 20 kV.

For studying the morphological changes of the composite specimens due to heating, samples were treated by a thermogravimetric analyzer at 300°C, 450°C, and 650°C. The obtained samples were then studied with a JOEL scanning electron microscope at an accelerating voltage of 10 kV.

For the fire-resistance tests, a pair of treated and untreated specimens [5 (R) × 30 (T) × 5 (L)] were placed in a V shape at an angle of 30° over the horizontal line. The specimens were then burned together at the tip of the V with a gas burner for 5 s by exposing it to the tip of the fire. The gas burner was then removed, and the specimens were allowed to burn until they disappeared. The gas burner was controlled carefully so the length of the flame was kept constant at 4 cm during the entire course of all tests. The carbonized composite specimen after burning was also studied with a JOEL scanning electron microscope.

Results and discussion

Na₂O-SiO₂ wood-inorganic composites

Table 1 shows the WPG and bulking coefficient for the obtained Na₂O-SiO₂ wood-inorganic composites with SM or SA. The WPGs of these composites were found to be more than 20.0%. On the other hand, the bulking coefficient of the composites with SA was higher than that of the composites with SM. These results suggest that a larger amount of inorganic gel was formed in the cell walls than in the cell lumens in the composites with SA compared to the composites with SM.

Table 1. Weight percent gain and bulking coefficient for Na₂O-SiO₂ wood-inorganic composites

Composite	Molar ratio					WPG (%)	B (%)
	MTMOS	MeOH	AcOH	SM	SA		
SiO ₂	0.03	1	0.01	0	0	11.0	6.6
Na ₂ O-SiO ₂ with SM	0.03	1	0.01	0.015	0	27.5	1.3
	0.03	1	0.01	0.030	0	28.4	2.4
	0.03	1	0.01	0.060	0	24.9	2.9
Na ₂ O-SiO ₂ with SA	0.03	1	0.01	0	0.015	24.7	2.5
	0.03	1	0.01	0	0.030	21.3	5.6
	0.03	1	0.01	0	0.060	32.5	8.5

MTMOS, methyltrimethoxysilane; MeOH, methanol; AcOH, acetic acid; SM, sodium methoxide; SA, sodium acetate; WPG, weight percent gain; B, bulking coefficient

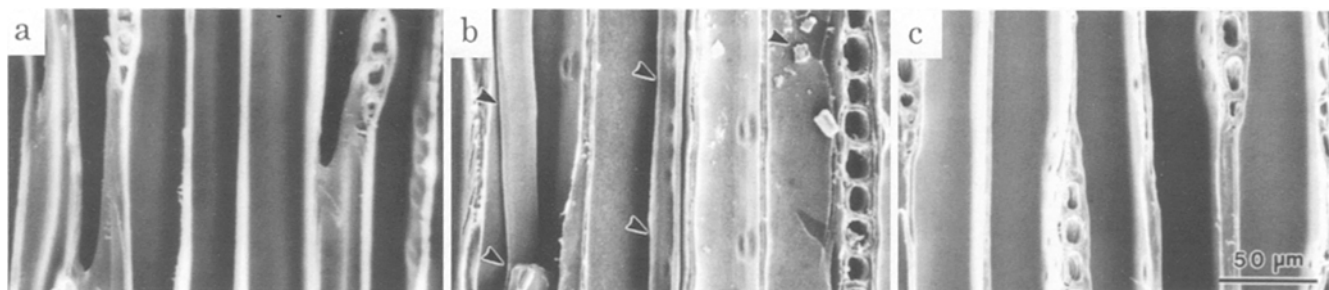


Fig. 1. Comparisons of scanning electron micrographs (SEM) of untreated wood (a); $\text{Na}_2\text{O-SiO}_2$ composites with sodium methoxide (SM) [methyltrimethoxysilane (MTMOS)/SM = 0.03/0.03, 29.1% weight percent gain in (WPG)] (b); and $\text{Na}_2\text{O-SiO}_2$ composites with sodium acetate (SA) (MTMOS/SA = 0.03/0.03, 21.2% WPG) (c)

Scanning electron microscopic (SEM) observations were therefore made for these composites, and the results are shown in Fig. 1, along with the results of untreated wood for comparison. In the composites with SM, the inorganic gel was found to be deposited in the cell lumens, as shown by the arrowheads. However, in the composites with SA, inorganic gel was not observed in the cell lumens, as in the untreated wood. The EDXA studies on the cell walls of these composites revealed the presence of silicon and sodium. Therefore, most of the inorganic gel is thought to be formed in the cell walls in the composites with SA. These SEM results and the EDXA studies confirmed the implication mentioned above. In previous papers,^{4-6,8} it was revealed that, compared with the inorganic gel formed in the cell lumens, the gel in the cell walls was more effective for property enhancement of wood with a small WPG of the gel. Therefore, the $\text{Na}_2\text{O-SiO}_2$ composites prepared with SA are preferable for enhancing the fire resistance of wood.

Thermal properties of $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites

Figure 2 shows the results of the thermogravimetric (TG) analysis on the $\text{Na}_2\text{O-SiO}_2$ composites with SM. The TG curves of the untreated wood and SiO_2 composites are also shown for comparison. On the TG curve of untreated wood, an abrupt decrease in its weight by flaming is observed between 300°C and 350°C. Subsequently, another characteristic decrease in its weight by glowing is observed between 350°C and 470°C. In comparison, the TG curves of the $\text{Na}_2\text{O-SiO}_2$ composites are shifted to the lower temperature during their first abrupt decrease in flaming. In addition, between 300°C and 600°C more residues resulted after flaming, with a gradual decrease to about 50% of their original weight. Above 600°C, the TG curves of these composites show an abrupt decrease by glowing. However, the TG curves for this decrease shifted to the higher temperature after an increase in the SM addition to the reaction medium.

Figure 3 shows the results of the differential thermal analysis (DTA) for the $\text{Na}_2\text{O-SiO}_2$ composites with SM compared with that for the untreated wood and SiO_2 composites. The prominent exothermic peaks for flaming and

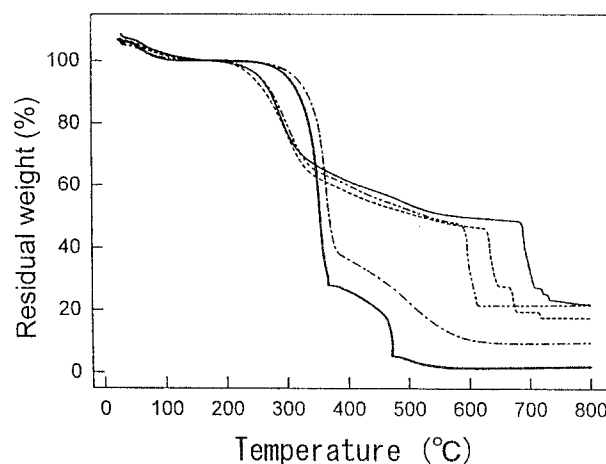


Fig. 2. Thermogravimetric (TG) curves for the $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites with SM. Heavy solid curve, untreated; long dashed/single short dashed, SiO_2 composites (11.0% WPG); long dashed/double short dashed, $\text{Na}_2\text{O-SiO}_2$ composites (MTMOS/SM = 0.03/0.015, 30.2% WPG); dashed, $\text{Na}_2\text{O-SiO}_2$ composites (MTMOS/SM = 0.03/0.030, 27.6% WPG); light solid, $\text{Na}_2\text{O-SiO}_2$ composites (MTMOS/SM = 0.03/0.060, 26.0% WPG)

glowing are observed, respectively, at 360°C and 440°C in the DTA of the untreated wood. In the SiO_2 composites these prominent peaks were weakened and broadened, indicating that some fire-resistant properties were enhanced. In the $\text{Na}_2\text{O-SiO}_2$ composites, however, the exothermic peak for flaming was further weakened, shifting its peak to the lower temperature, and only a broad exothermic peak hill is observed at about 300°C. These results indicated the enhanced fire resistance to flaming in the $\text{Na}_2\text{O-SiO}_2$ composites. On the DTA curves of the $\text{Na}_2\text{O-SiO}_2$ composites at the higher temperature (>600°C) prominent peaks are observed that are due to glowing. In addition, the peak temperature shifted to the higher temperature when the SM addition to the reaction medium was increased. This shift corresponded to that of the temperature of the abrupt weight decrease in the TG curves, as shown in Fig. 2.

Based on these results, it was thought that the $\text{Na}_2\text{O-SiO}_2$ composites can raise the glowing temperature, despite its exothermic behaviors. In particular, the composites prepared from the reaction medium with a molar ratio of

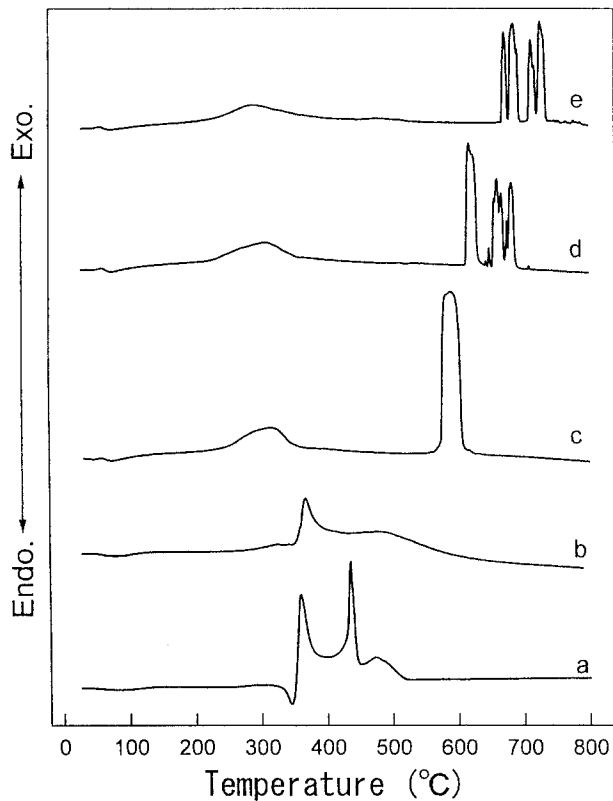


Fig. 3. Differential thermal analysis (DTA) curves for the $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites with SM. *a*, Untreated; *b*, SiO_2 composites (11.0% WPG); *c*, $\text{Na}_2\text{O-SiO}_2$ composites (MTMOS/SM = 0.03/0.015, 30.2% WPG); *d* $\text{Na}_2\text{O-SiO}_2$ composites (MTMOS/SM = 0.03/0.030, 27.6% WPG); *e* $\text{Na}_2\text{O-SiO}_2$ composites (MTMOS/SM = 0.03/0.060, 26.0% WPG). Endo., Exo., endothermic, exothermic

0.06/0.03 SM/MTMOS surprisingly raised the glowing temperature to about 700°C.

Figure 4 shows the results of the TG analysis for the $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites with SA. The TG curves of the untreated wood and the $\text{Na}_2\text{O-SiO}_2$ composites with SM are shown for comparison. Compared with the untreated wood, the TG curve of the $\text{Na}_2\text{O-SiO}_2$ composite with SA shifts to the lower temperature for flaming. In addition, between 300°C and 600°C more residue resulted after flaming. As a result, the glowing temperature is elevated to about 600°C, as observed for the composites with SM. Closer inspection indicates that the $\text{Na}_2\text{O-SiO}_2$ composites with SA have a lower residual weight after flaming than the composites with SM. Considering the difference in the WPGs for these composites, the fire-resistant effect of these composites can be assumed to be essentially the same.

Figure 5 shows the results of the DTA for the $\text{Na}_2\text{O-SiO}_2$ composites with SA, compared with untreated wood and $\text{Na}_2\text{O-SiO}_2$ composites with SM. The prominent exothermic peak observed for the untreated wood for flaming is weakened, and the peak for glowing has shifted to a higher temperature (about 650°C), as was seen for composites with SM. Based on these results, it is obvious that the $\text{Na}_2\text{O-SiO}_2$ composites with SA have a great fire-

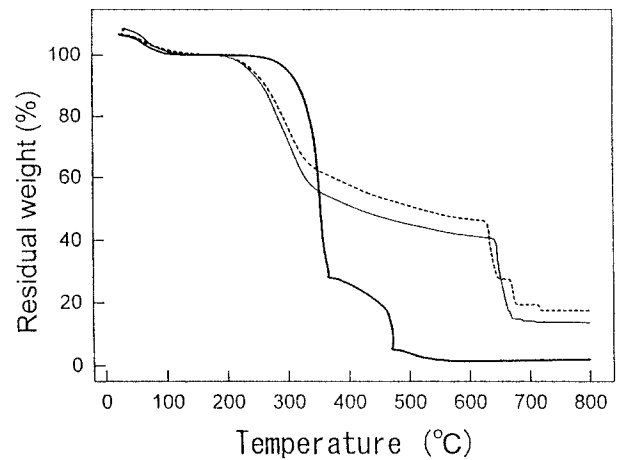


Fig. 4. TG curves for $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites with SA. *Heavy solid curve*, untreated; *dashed curve*, $\text{Na}_2\text{O-SiO}_2$ composites with SM (MTMOS/SM = 0.03/0.03, 27.6% WPG); *light solid curve*, $\text{Na}_2\text{O-SiO}_2$ composites with SA (MTMOS/SA = 0.03/0.03, 21.2% WPG)

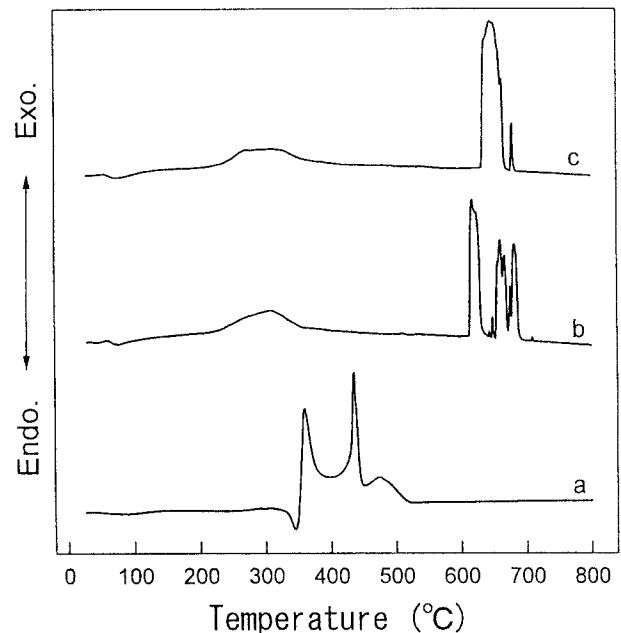


Fig. 5. DTA curves for the $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites with SA. *a*, Untreated; *b*, $\text{Na}_2\text{O-SiO}_2$ composites with SM (MTMOS/SM = 0.03/0.03, 27.6% WPG); *c*, $\text{Na}_2\text{O-SiO}_2$ composites with SA (MTMOS/SA = 0.03/0.03, 21.2% WPG)

resistant effect as observed for the $\text{Na}_2\text{O-SiO}_2$ composites with SM.

These results indicating enhanced fire resistance of the $\text{Na}_2\text{O-SiO}_2$ composites are confirmed in Fig. 6, which shows the results of the fire-resistance tests. The untreated specimens became shorter with ashes due to combustion. Compared with this, the SiO_2 composites revealed some fire resistance with a longer carbonized residue. However, $\text{Na}_2\text{O-SiO}_2$ composites exhibited much more resistance to burning with longer but less carbonized residue.

Mechanisms of fire resistance of Na₂O-SiO₂ composites

In previous papers,⁹⁻¹¹ the TG curves for flaming of the binary SiO₂-P₂O₅ composites were found to have shifted to the lower temperature compared with that of the untreated wood. This was due to the enhanced dehydration reaction with the phosphorus compound. A basic sodium compound is known to have a similar effect on the phosphorus compound.¹⁶ Owing to this chemical effect, TG curves for flaming of the binary Na₂O-SiO₂ composites shifted to a lower temperature, as in Figs. 2 and 4; thus, these composites could have attained enhanced fire resistance to flaming.

To clarify the mechanisms of fire resistance of the Na₂O-SiO₂ composites for glowing, SEM observations were made on the composites treated at 300°C, 450°C, and 650°C, as shown in Fig. 7. Although some inorganic gel can be seen on the surface of the cell walls in the composites at room temperature, those were not observed in the composites

treated at 300°C and 450°C. However, at 650°C these components can be seen again on the surface of the cell walls. Based on these results, it is assumed that the gel formed in wood would have melted and covered the surfaces of wood cells with glassy layers as the temperature increased. This glassy layer could have prevented the cell wall components from being volatile products of combustion and, further, from being exposed to oxygen. Therefore, the fire resistance to glowing could be achieved successfully. However, as the temperature was raised further, the glassy layer shrank to the granules as in Fig. 7e. With this shrinkage of the glassy layer covering the cell walls, oxygen would be accessible to the cell wall components of wood, and glowing would subsequently occur.

To study morphological changes further, more intensive SEM observations were made on the composites after fire-resistance tests and were compared to those of untreated wood (Fig. 8). The Na₂O-SiO₂ composites were found to form an intumescent structure on the surface of the cell walls that was not observed with untreated wood. This intumescent structure was not, however, observed in the composites treated by the thermogravimetric analyzer, as shown in Fig. 7. This difference may be due to the heating rate. When the Na₂O-SiO₂ composites were treated at a lower heating rate (e.g., 20°C/min) a variety of reactions occurred slowly during the process of heating, such as dehydration of wood by Na₂O gel, vaporization of some volatile compounds, and melting of the gel, with formation of a glassy layer over the wood. With rapid heating, as occurs with exposure to a flame, these reactions take place instantaneously and vigorously. Therefore, an intumescent structure on the surface of the cell walls in the Na₂O-SiO₂ composites might be formed by glazing of the melted gel

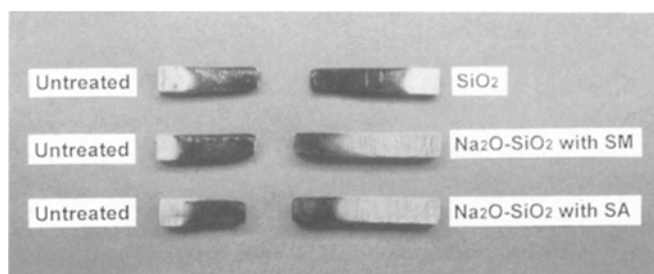


Fig. 6. Comparison of burned specimens after the fire-resistance test. Untreated wood specimens (**left**) versus SiO₂, Na₂O-SiO₂ wood-inorganic composites with SM, and Na₂O-SiO₂ wood-inorganic composites with SA

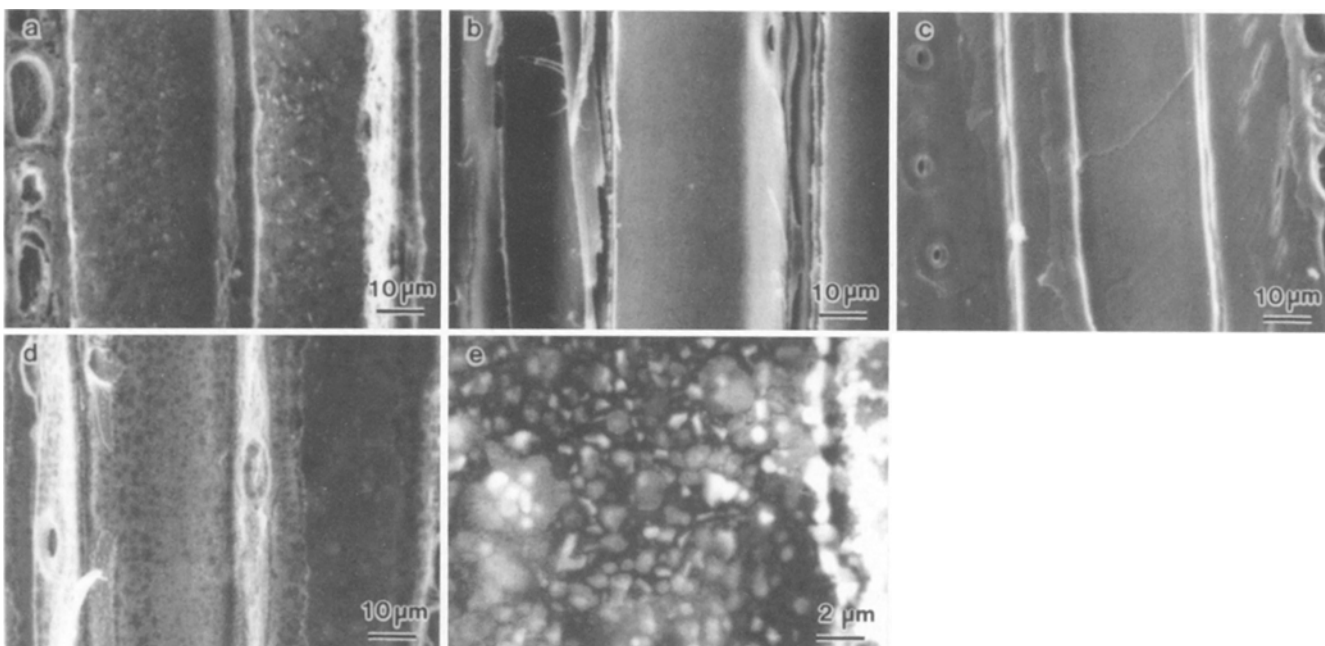


Fig. 7. Comparisons among the Na₂O-SiO₂ wood-inorganic composites with SM (MTMOS/SM = 0.03/0.06, 26.0% WPG) treated at various temperatures. **a** Room temperature. **b** 300°C. **c** 450°C. **d** 650°C. **e** Magnified view of **d**

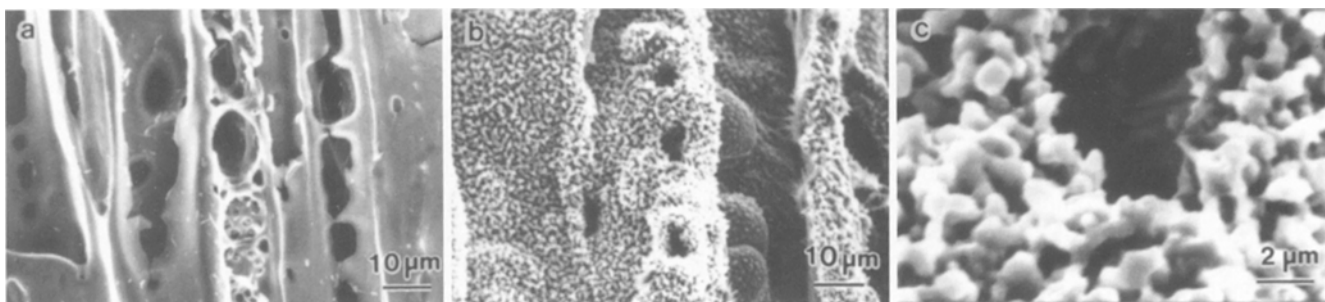


Fig. 8. Comparisons between the $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites with SM and untreated wood after fire-resistance tests. **a** Untreated wood. **b** $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites (MTMOS/SM = 0.03/0.06, 26.0% WPG). **c** Magnified view of **b**

Table 2. pH of the reaction media for $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites

Reaction	Molar ratio						pH
	MTMOS	MeOH	AcOH	SM	SA	H_2O	
1	0.03	1	0.01	0.03	0	0	8.8
2	0.03	1	0.01	0.03	0	0.3	11.4
3	0.03	1	0.01	0	0.03	0	6.2
4	0.03	1	0.01	0	0.03	0.3	6.7

with vaporization of some volatile compounds. Such an intumescent structure is known to enhance the fire-resistant properties by insulating the wood.^{16,17} The $\text{Na}_2\text{O-SiO}_2$ composites therefore could attain their enhanced fire resistance (as shown by fire-resistance tests) not only by the coating effects of the glassy layer mentioned above but by the insulating effects of an intumescent structure formed over the surfaces of the wood cell walls in the composites. These mechanisms for fire resistance are considered similar to those of $\text{Na}_2\text{O-SiO}_2$ composites with SM and those with SA because the thermal properties in TG and DTA analyses were essentially the same.

pH of reaction media for $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites

Table 2 shows the pH of the reaction media for the $\text{Na}_2\text{O-SiO}_2$ composites with SM and SA (reactions 1 and 3). The molar ratio of the chemical components is also shown. Although a reaction medium with SM (reaction 1) is basic, a reaction medium with SA (reaction 3) is weakly acidic. During impregnation of these reaction media into the moisture-conditioned wood to obtain the $\text{Na}_2\text{O-SiO}_2$ wood-inorganic composites, these reaction media are mixed with bound water in the cell wall. Therefore, water was added to these solutions and the pH of the obtained solutions was measured, as shown in Table 2 (reactions 2 and 4). It was consequently found that the reaction 1 solution becomes strongly basic by addition of water, whereas the pH of the reaction 4 solution remains almost unchanged, with weak acidity. In a report on the alkaline strain on wood,¹⁸ discoloration became marked by basic treatment of the solution over about pH 11. Therefore, a reaction medium for the

$\text{Na}_2\text{O-SiO}_2$ composites with SM possibly causes the discoloration during the impregnation treatment. Based on these lines of evidence, the reaction medium with SA is preferable for preparing the $\text{Na}_2\text{O-SiO}_2$ composites, compared to that with SM.

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