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Author(s)	Miyafuji, Hisashi
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HISASHI MIYAFUJI

2000

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Preface

Recently, energy and environmental issues such as an exhaustion of fossil resources, a destruction of forest, and a global warming are getting to be serious. People all over the world, therefore, pay much attention to these problems, and many researches or investigations are now made to solve these problems. Under these circumstances, increasing attentions have been focused on the biomass resources as renewable and environmentally friendly materials.

Wood as most important and useful biomass resources has been utilized for various uses since ancient time. Even now, wood is considered to be very useful and essential materials, especially for residential buildings because of its natural beauty and excellence in properties, such as high specific strength, heat insulation, and an ease to handle. However, it has some unfavorable end-products properties in dimensional stability, combustibility, and biodeterioration. Particularly, the combustibility of wood in the residential buildings are thought to be a concern for residents. In the case of the fire on their buildings, they would lose not only their fortunes but also their lives. Therefore, some restrictions on the use of wood for residential buildings are imposed. If enhancement on the fire-resistance of wood could be achieved, wood would not only be free from a danger of the fire but also could be used positively. Therefore, to overcome this disadvantageous characteristics of wood, many attempts have been made.

For enhancing the fire-resistance of wood, phosphorous compounds are well-known to be effective. Many researches have made on the fire-resistance of wood treated with phosphorous compounds such as phosphoric acid, phosphonate or organophosphorous compounds (Browne 1958, Kishore and Mohandas 1982, Ishihara 1987, Hagio *et al.* 1988, Ellis *et al.* 1989, Ellis 1991, Getto and Ishihara 1998). Boron compounds are also well-known as fire-retardants. Wood or cellulosic materials treated with boric acid or borate are reported to have a good fire-resistance for flaming and glowing (Browne 1958, Ishihara 1989, Su et al. 1995, 1997a, 1997b). However, chemically treated woods have sometimes a problem in the stability of the chemicals deposited in the wood. Efforts were, thus, made for enhancement of the stability of the chemicals with keeping their fire-resistance (Peylo and Willeintner 1995).

Recently, inorganic modification of wood has been developed as promising method for enhancing the properties of wood. Some studies were made on the enhanced properties of the wood-inorganic composites prepared by various methods.

The wood-inorganic composites with barium phosphate or barium hydrogen phosphate by the double diffusion process is one of the good examples to show enhancement of wood properties (Nishimoto *et al.* 1988). A similar trial is also reported to prepare wood inorganic composites from water glass solution system or colloidal silica solution system to form the inorganic deposits in wood (Furuno *et al.* 1991, 1993, 1997, 1999, Yamaguchi 1994, Yamaguchi and Ostman 1996). Although the obtained wood-inorganic composites from the methods mentioned above can achieve the high fire-resistance, the porous structure which is one of the advantageous characteristics of wood is lost with much inorganic substances deposited in the cell lumens.

As another trial, a sol-gel process has been applied to prepare wood-inorganic composites (Saka *et al.* 1992a, Saka and Kitazawa 1993, Ogiso and Saka 1993, Saka and Yakake 1993, Saka 1995, Saka and Tanno 1996, Saka and Ueno 1997), and inorganic substances were found to be distributed differently in wood among different metal alkoxides with moisture-conditioned wood or water-saturated wood (Saka *et al.* 1992, Saka and Kitazawa 1993, Ogiso and Saka 1993, Saka and Yakake 1993). From a comparative study for the several composites obtained, SiO_2 wood-inorganic composites with moisture-conditioned wood have been one of the most promising ones in property enhancement, with specifically deposited SiO_2 gel within the cell walls. It is also fascinating that SiO_2 gel are environmentally friendly materials.

However, to enhance further the properties of the SiO_2 wood-inorganic composites, some silane coupling agents were used to prepare chemically modified wood prior to its inorganic modification with SiO_2 gel. The prepared chemically modified wood-inorganic composites in which the SiO_2 gel is condensed with an isocyanate or an epoxy type silane coupling agent covalently bonding with wood, were found to be more effective for dimensional stabilization and fire-resistance (Ogiso and Saka 1994).

More recently, some silicon alkoxides with the antimicrobial functional group were applied to the reaction system for SiO_2 composites to prepare the antimicrobial wood-inorganic composites. The obtained wood-inorganic composites revealed some antimicrobial activities, but the use of the property enhancer with hydrophobic perfluoroalkyl chain could provide water-repellent property to the composites which has, furthermore, improved its activities against both white-rot and brown-rot fungi (Tanno *et al.* 1997, 1998).

In this dissertation, efforts were made for enhancing the fire-resisting properties of wood to prepare the wood-inorganic composites by the sol-gel process. Various wood-inorganic composites from binary or ternary reaction systems were prepared.

In Chapter 1, the preparation of various wood-inorganic composites in mono-reaction system by the metal alkoxides and their thermal properties were studied by thermogravimetric (TG) analysis and differential thermal analysis (DTA).

In Chapter 2, some titanium alkoxides and chelates which have the lowere rate of hydrolysis and subsequent polycondensation were used for preparing TiO_2 wood-inorganic composites with the TiO_2 gel deposited in the cell wall. The topochemical effects of TiO_2 gel on the properties enhancement were studied by evaluating the thermal properties of the prepared composites.

In Chapter 3, trimethylphosphite (TMP) or/and trimethylborate (TMB) was/were applied to a reaction system for SiO_2 wood-inorganic composites to prepare binary SiO_2-P_2O_5, SiO_2-B_2O_3 and ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites. The prepared composites were, then, studied on their thermal properties by thermal analyses, and the effects of the P_2O_5 and B_2O_3 gels were evaluated on property enhancement of the SiO_2 wood-inorganic composites.

In Chapter 4, some siloxane alkoxide oligomers with phosphorous and/or boric hydroxide residues were prepared and applied for preparing the SiO_2-P_2O_5-B_2O_3 wood-inorganic composites to improve the environmental safety for the preparation of the composites. Furthermore, 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) as a property enhancer was added to the reaction system to enhance the stability of the SiO_2-P_2O_5-B_2O_3 gels in the composites. The prepared composites were studied on the thermal properties and the stability of the gel.

In Chapter 5, to elucidate a mechanism of the property-enhancement for the wood-inorganic composites with HFOETMOS, various HFOETMOS woods and HFOETMOS-SiO_2 wood-inorganic composites were prepared. By evaluating their water-repellency and the scanning electron microscopy coupled with an energy-dispersive X-ray analysis (SEM-EDXA) on the prepared composites, the topochemical effects of HFOETMOS on the water-repellency were studied.

In Chapter 6, sodium methoxide (SM) or sodium acetate (SA) was applied to a reaction system for SiO_2 wood-inorganic composites to prepare binary

Na_2O-SiO_2 wood-inorganic composites. The prepared composites were studied their thermal properties by thermal analyses and elucidated the mechanisms their fire-resistance by the scanning electron microscopy (SEM) observations.

Chapter 1
Wood-Inorganic Composites from Various Metal Alkoxides

1.1 INTRODUCTION

For enhancing the wood properties, the sol-gel process in binary or ternary reaction system was thought to be applied for preparing wood-inorganic composites. However, prior to this trial, the wood-inorganic composites from various metal alkoxides in mono-reaction system must be studied. Therefore, in this chapter, the preparation of various wood-inorganic composites in mono-reaction system and their thermal properties were studied by thermogravimetric (TG) analysis and differential thermal analysis (DTA).

1.2 MATERIALS AND METHODS

1.2.1 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 (24 h) and water (24 h) in a Soxhlet apparatus. Extracted wood specimens were then oven-dried, and their oven-dried weights were measured. To prepare the moisture-conditioned wood specimens with 20 to 25% moisture contents, oven-dried specimens were placed in a desiccator for three weeks at 20 ℃ in which the relative humidity was controlled to be 98% by a saturated salt solution of K_2SO_4.

1.2.2 Preparation of wood-inorganic composites

Solutions with a molar ratio of 1:1:0.01 in tetraethoxysilane (TEOS), ethanol, and acetic acid were prepared for SiO_2 wood-inorganic composites. To prepare P_2O_5 and B_2O_3 wood-inorganic composites, trimethylphosphite (TMP) and trimethylborate (TMB) were, respectively, used instead of TEOS in the above reaction system. On the other hand, a solution with a molar ratio of 0.03:1:0.01 in tetraisopropoxytitanium (TPT), isopropanol, and acetic acid was prepared for TiO_2 wood-inorganic composites, and a solution with a molar ratio of 0.03:1 in aluminumtri-*s*-butoxide, and isopropanol was prepared for Al_2O_3 wood-inorganic composites. To prepare a solution for ZrO_2 wood-inorganic composites, zirconiumethoxide and ethanol were mixed and stirred at 50 ℃ for 1 h. Subsequently, this mixture was allowed to stand overnight at room temperature. To this solution (75 ml) for ZrO_2 wood-inorganic composites, 0.15 ml of acetic acid was added as a catalyst.

Into moisture-conditioned specimens, the prepared solutions described above were impregnated at 20 ℃ under a reduced pressure (15 mmHg) for three days. The treated specimens were then placed in an oven controlled to be 65 ℃ for 24 h and 105 ℃ for another 24 h for aging of the gel.

1.2.3 Evaluation of wood-inorganic composites

The weight percent gain (WPG) of the composites was determined on an oven-dried weight basis as shown in an equation of (1-1), by measuring the oven-dried weights of the extractive-free untreated specimen (Wu) and the composite specimen (Wt).

$$\mathrm{WPG}(\%)=(\mathrm{Wt}-\mathrm{Wu})/\mathrm{Wu}\times 100 \qquad (1\text{-}1)$$

For testing thermal properties, about 8 mg composite specimens were studied with a thermogravimetric analyzer, Shimadzu TGA-50, and a differential thermal analyzer, Shimadzu DTA-50, with a flow of dried air (50 ml/min). The temperature was raised from 20 to 800 ℃ at a heating rate of 20 ℃/min.

1.3 RESULTS AND DISCUSSION

1.3.1 Thermal properties of various wood-inorganic composites

Table 1-1 shows the WPGs of various wood-inorganic composites prepared from various metal alkoxides. For these composites, the thermal properties were evaluated by thermogravimetric (TG) analysis and differential thermal analysis (DTA).

Table 1-1. WPGs of various wood-inorganic composites.

Composites	WPGs(%)
SiO_2	8.4
B_2O_3	9.5
P_2O_5	9.4
TiO_2	17.4
ZrO_2	3.2
Al_2O_3	5.0

Figure 1-1 shows the TG curves of various wood-inorganic composites. In the TG curves of the untreated wood specimens, the abrupt decrease in its weight is observed at the temperature range between 300 and 350 ℃. This is known to be due to a flaming of wood components with air. Compared with this, the TG curve of the SiO_2 and B_2O_3 composites are shifted to the upper temperature during the flaming. On the other hand, the TG curve of the P_2O_5 composite is obviously shifted to the lower temperature during the flaming.

In the untreated wood specimens, the TG curve reveals another characteristic phenomenon after flaming ; in the temperature range between 360 and 470 ℃, so-called glowing takes place. Compared with this, the TG curve of the SiO_2 composites shows the higher residue after flaming at about 370 ℃ and its gradual decrease can be seen in between 370 and 550 ℃, improving the thermal properties of wood with SiO_2 gel.

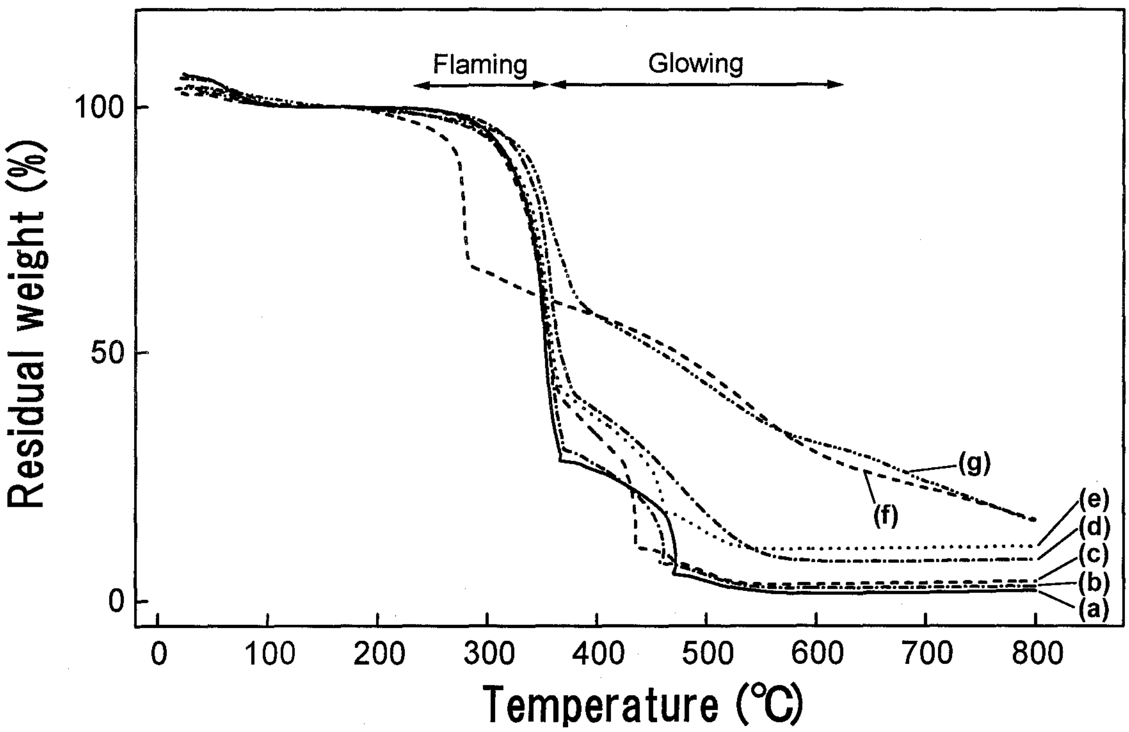


Fig. 1-1. TG curves for various wood-inorganic composites.
(a) Untreated (b) Al_2O_3 (5.0 WPG) (c) ZrO_2 (3.2 WPG)
(d) SiO_2 (8.4 WPG) (e) TiO_2 (17.4 WPG)
(f) P_2O_5 (8.4 WPG) (g) B_2O_3 (9.5 WPG)

The TG curves of the P_2O_5 and B_2O_3 composites also show the much higher residue after flaming and its gradual decrease can be seen at the glowing. The TG curve of the TiO_2 composites resembles that of the SiO_2 composites. However, the TiO_2 composites do not improve the thermal properties of wood so effectively as the SiO_2 composites because the WPG of the TiO_2 composites is higher than that of the SiO_2 composites. In the ZrO_2 composites, the TG curve shows the higher residue after flaming. But the abrupt decrease in its weight is observed at the glowing, promoting the combustion of wood. The TG curve of the Al_2O_3 composites is likely to be that of the untreated wood. This indicates that the Al_2O_3 composites do not have the fire-resistance.

For the various wood-inorganic composites studied, DTA analysis was

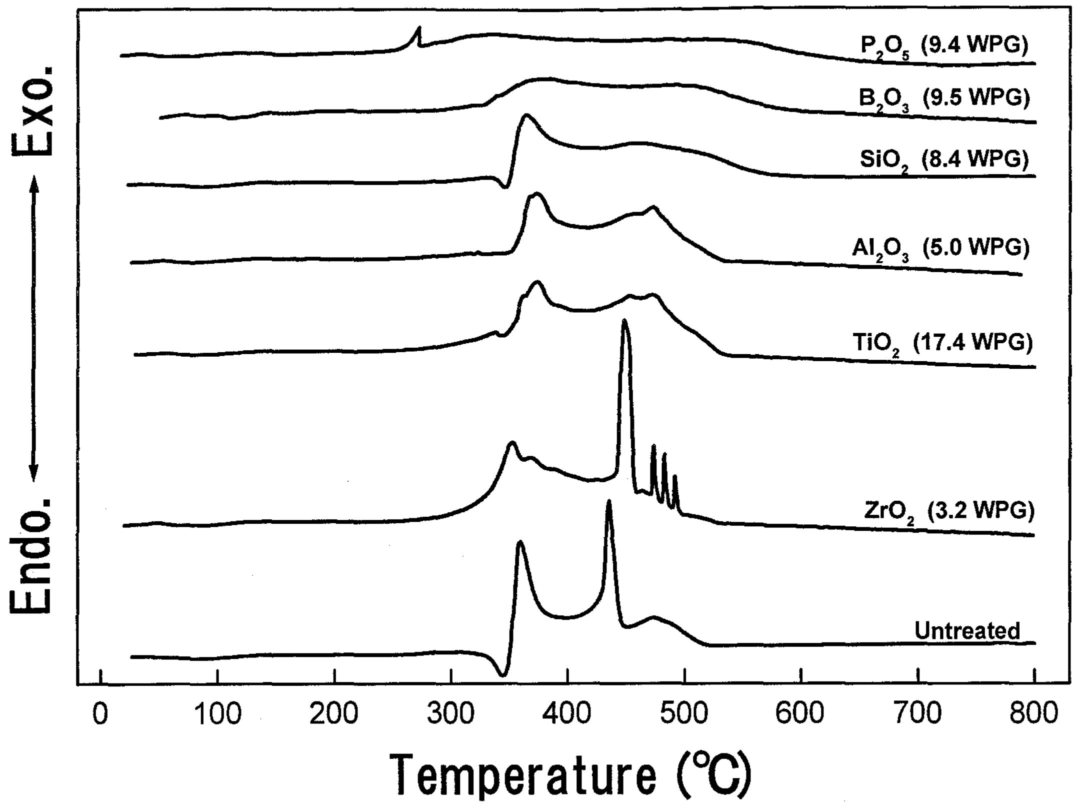


Fig. 1-2. DTA curves for various wood-inorganic composites.

also made and the DTA curves obtained are shown in Fig. 1-2. In the DTA curve of the untreated wood specimens, the first endothermic peak at about 360 ℃ is due to a pyrolysis of wood, and it was weakened for all wood-inorganic composites. It indicates that the inorganic modification of wood can restrain the pyrolysis of wood.

Again, in the DTA curve of untreated wood specimens, two exothermic peaks due to oxidation are evident which correspond to the flaming and glowing. Such exothermic peaks are weakened or disappear through inorganic modification of wood. In SiO_2 composites, an exothermic peak was weakened and broadened, indicating some resistance against flaming. In more elevated temperature ranges, the prominent peak disappears and a broader exothermic hill is observed to the higher temperature, compared with untreated wood specimens.

Such a fire-resisting effect is more evident in the B_2O_3 composites, and an exothermic peak observed at 380 ℃ in SiO_2 composites has disappeared in the B_2O_3 composites and one broad exothermic curve continued up to about 600 ℃. In the P_2O_5 composites, a similar fire-resisting effect is evident in which no prominent exothermic peaks are observed but only a slight peak is present at about 280 ℃. Furthermore, a very broad exothermic hill is continued up to over 600℃, indicating a strong resistance of the composites against the thermal attack and a striking effect of P_2O_5 gel on the fire-resistance.

On the other hand, in the ZrO_2 composites, although the exothermic peak for flaming is weakened, the prominent peak is observed at the glowing, indicating no resistance against the thermal attack. In the TiO_2 and Al_2O_3 composites, the DTA curves resemble that of SiO_2 composites, but the peaks for glowing are slightly higher, compared with SiO_2 composites. Only from the results of the obtained DTA curves, TiO_2 and Al_2O_3 composites seem to have some fire-resisting effects as in SiO_2 composites. However, considering the results of the TG analyses, the fire-resisting effects of these composites are not so high.

1.4 SUMMARY

In this chapter, various wood-inorganic composites were prepared from mono-reaction systems and studied on their thermal properties by thermal analyses. The TG curves of the SiO_2, P_2O_5 and B_2O_3 composites show the higher residue after flaming and their gradual decrease can be seen during their glowing, compared with the untreated wood and some other composites. In the DTA curves of SiO_2, P_2O_5 and B_2O_3 composites, the prominent exothermic peaks for flaming and glowing as shown in untreated wood and some other composites were not observed. From these results, it can be concluded that the SiO_2, P_2O_5, and B_2O_3 composites can improve the thermal properties of wood, and have a good fire-resistance with a small WPG.

Therefore, as a next trial, SiO_2-P_2O_5-B_2O_3 composites in binary or ternary reaction system were studied. Before that, in following chapter, efforts were made for enhancing the fire-resisting property of TiO_2 composites which did not show so high fire-resistance. The topochemical effects of TiO_2 gel for the property enhancement were also studied

Chapter 2

Several TiO_2 Wood-Inorganic Composites from Titanium Alkoxides and Chelates

2.1 INTRODUCTION

To enhance the properties of wood, a sol-gel process has been applied with some metal alkoxides to prepare wood-inorganic composites. On the prepared various wood-inorganic composites, inorganic substances were found to be distributed differently within the wood cells (Saka *et al.* 1992a, Ogiso and Saka 1993, Saka and Yakake 1993). Recent studies indicated that this is due to a difference in the rate of hydrolysis and subsequent polycondensation (Saka and Kitazawa 1993, Saka 1995). It is also revealed that topochemical effects of the inorganic substances exist for the wood property enhancement, and that SiO_2 wood-inorganic composites in which inorganic substances are formed within the cell walls were found to enhance the properties of wood effectively (Ogiso and Saka 1993).

Unlike SiO_2 wood-inorganic composites, TiO_2 wood-inorganic composites could not be improved in their properties with tetraisopropoxytitanium (TPT). This is because TPT is rapidly hydrolyzed and polycondensed so that in a moisture-conditioned specimens, the TiO_2 gel is formed within the cell lumens before TPT is impregnated into the cell walls (Saka and Yakake 1993).

Therefore, in this chapter, titanium alkoxides or titanium chelates which have the lower rate of hydrolysis and subsequent polycondensation than TPT were selected for preparing TiO_2 wood-inorganic composites so as for the TiO_2 gel to be formed within the cell walls. On the obtained composites, their thermal properties were studied by thermogravimetric (TG) analysis and differential thermal analysis (DTA) to study topochemistry of wood-inorganic composites for the property enhancement.

2.2 MATERIALS AND METHODS

2.2.1 Wood specimens

The wood specimens were prepared by the same procedure described in Chapter 1.

2.2.2 Preparation of wood-inorganic composites

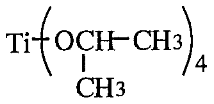
The reagents used in this study for preparing TiO_2 composites are shown in Fig. 2-1 to be tetraisopropoxytitanium (TPT), tetra-*n*-butoxytitanium (TBT) and tetrakis(2-ethylhexyloxy)titanium (TOT) as titanium alkoxides, and diisopropoxybis(acetylacetonato)titanium (TAA) and di-*n*-butoxybis(triethanolaminato)titanium (TAT) as titanium chelates, all of which were provided from Nippon Soda Co., Ltd. These reagents were dissolved in alcohol with 20wt% in concentration for preparing the wood-inorganic composites. The combinations of these reagents with alcohols adopted were TPT/isopropanol, TBT/*n*-butanol, TOT/*n*-butanol, TAA/isopropanol, and TAT/isopropanol.

The prepared solutions described above were then impregnated into moisture-conditioned specimens at 20 ℃ under a reduced pressure (15 mmHg) for three days. The impregnated specimens were then placed in an oven controlled to be 65 ℃ for 24 h and 105 ℃ for another 24 h for aging of the gel.

2.2.3 Evaluation of wood-inorganic composites

The weight percent gain (WPG) of the composites were determined by the same procedure described in Chapter 1.

The bulking coefficient (B) of the composite was determined on an oven-dried basis as shown in an equation of (2-1), by measuring the oven-dried length of the extractive-free untreated specimens and the composite.

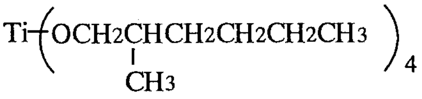


$\mathrm{Ti{\left(OCH(CH_3){-}CH_3\right)}_4}$

Tetraisopropoxytitanium (TPT)

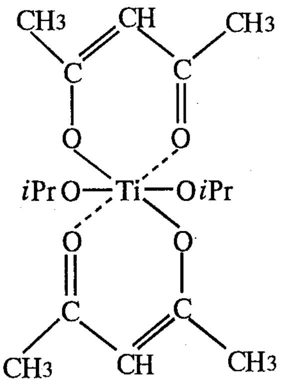
$\mathrm{Ti(OCH_2CH_2CH_2CH_3)_4}$

Tetra-*n*-butoxytitanium (TBT)

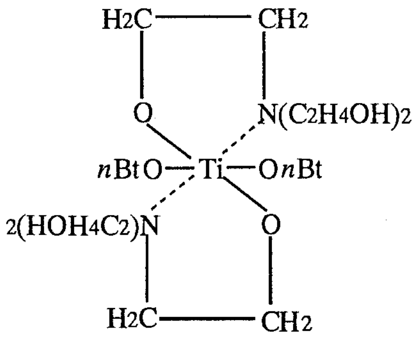


$\mathrm{Ti{\left(OCH_2CH(CH_3)CH_2CH_2CH_2CH_3\right)}_4}$

Tetrakis(2-ethylhexyloxy)titanium (TOT)



Diisopropoxy bis(acetylacetonato)titanium (TAA)



Di-n-butoxy bis(triethanolaminato)titanium (TAT)

Fig. 2-1. Chemical structure of titanium alkoxides and titanium chelates for various TiO_2 composites.

$$B(\%)=(Vc-Vu)/Vu \times 100 \qquad (2\text{-}1)$$

where Vc is an oven-dried volume of composite specimen and Vu is an oven-dried volume of untreated specimen.

For an energy dispersive X-ray analysis, the block specimens of the composites surfaced with a freeze-microtome, were mounted on a carbon specimen-holder, carbon-coated, and studied with a JOEL scanning electron microscope (JSM-T330A) coupled with EDAX[*1] 9100/70 energy dispersive X-ray spectrometer (SEM-EDXA) for its morphology and distributions of TiO_2 gel in the composite.

The determination of the antiswelling efficiency (ASE) was made on prepared composite specimens after being subjected to three days of soaking in distilled water.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made on the composites by the same procedure described in Chapter 1. Furthermore, for identifying the evolved gas during burning, composites were studied with Shimadzu thermogravimetric analyzer/gas chromatograph-mass spectrometer combined system (TG/GC-MS)-QP 5000A, with a flow of dried gas which consists of oxygen and helium as a pseudo-air with their volumetric ratio of 21:79.

2.3 RESULTS AND DISCUSSION

2.3.1 Distribution of the inorganic substances

Table 2-1 shows the WPG, B, and ASE for the prepared TiO_2 wood-inorganic composites in this study.

Generally, titanium chelates have the lower rate in hydrolysis than titanium alkoxides, and the titanium alkoxides with the larger alkoxyl groups have the lower rate in its hydrolysis (Yatsuma 1987). The hydrolysis rate of the reagents used in this study is, therefore, increased in the following order;

[*1] EDAX is a trade name, whereas EDXA found in the text refers to energy dispersive X-ray analysis.

Table 2-1. WPG, B and ASE of the various TiO_2 wood-inorganic composites.

Reagent	WPG(%)	B(%)	ASE(%)
TPT[a]	22.8	-	-5.0
TBT	18.1	3.6	22.7
TOT	18.3	7.2	38.4
TAA	17.1	3.3	22.3
TAT	24.7	8.9	41.0

[a] Previous work (Saka and Yakake 1993)

$$\mathrm{TAA} \fallingdotseq \mathrm{TAT} < \mathrm{TOT} < \mathrm{TBT} < \mathrm{TPT}$$

The difference in the hydrolysis rate above seems to result in the different distribution of inorganic substances within the wood cells. Figure 2-2 (a, b) shows that, as moisture-conditioned wood specimens are treated with TPT/isopropanol solution (Saka and Yakake 1993, Saka and Kitazawa 1993), the TiO_2 gel is formed only within the cell lumens, as revealed by Ti-Kα X-ray mapping. This is due to a rapid hydrolysis and polycondensation of TPT. For other cases, the results are shown in Fig. 2-2 (c-f), in which the TiO_2 gel can be seen in the cell lumens in TBT and TOT composites, whereas in TAA and TAT composites, no deposits are observed. However, SEM-EDXA observations clearly revealed the presence of TiO_2 gel in the cell walls of these latter composites.

These lines of evidence agree well with the above order of the hydrolysis rate of the reagents used, because the reagent with the lower rate in hydrolysis can be penetrated into the cell walls before its hydrolysis and subsequent polycondensation, resulting in the formation of TiO_2 gel within the cell walls.

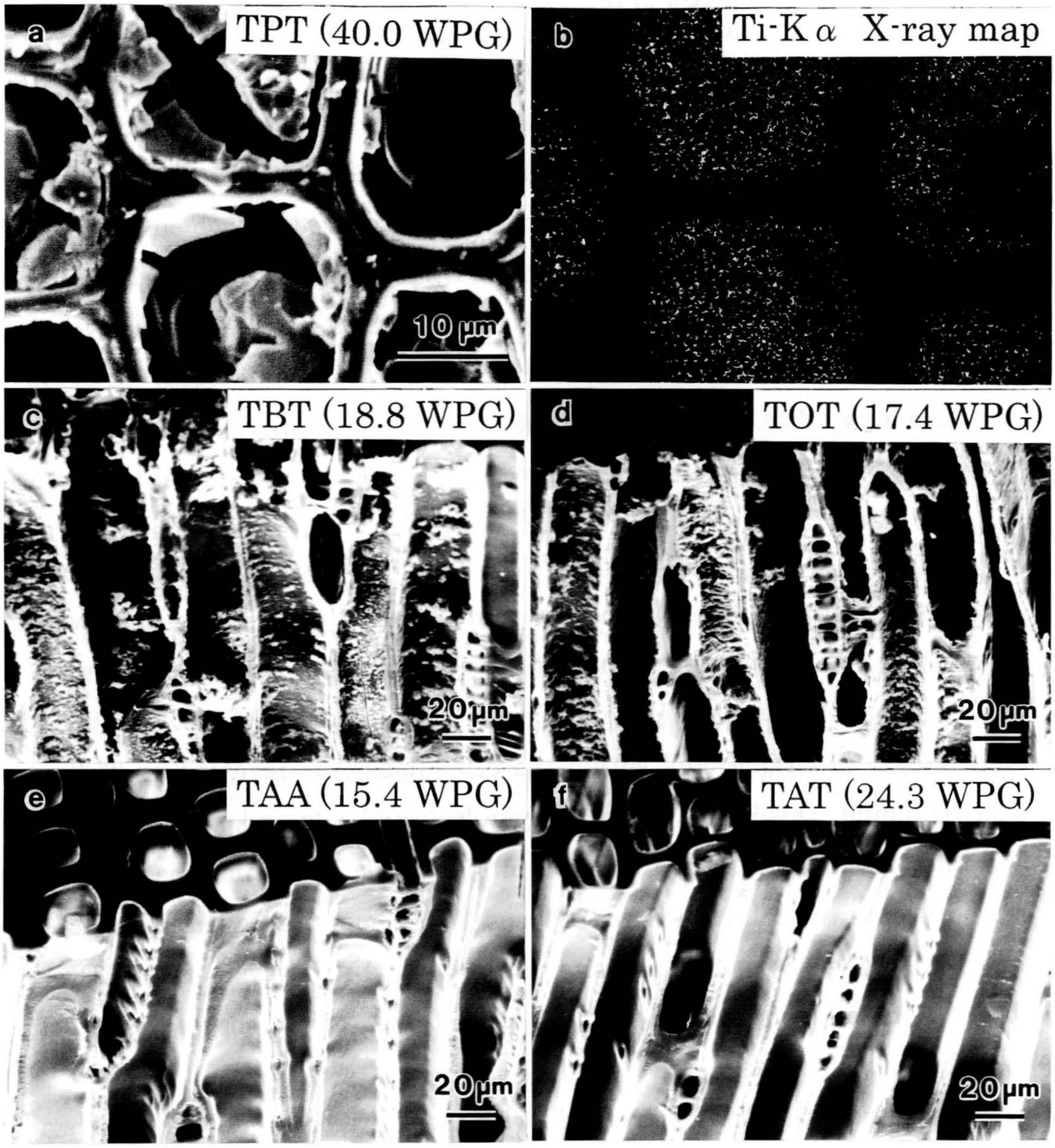


Fig. 2-2. SEM micrographs of various wood-inorganic composites.
(a)TPT composite (40.0 WPG) (b)Ti-Kα X-ray map of TPT composites
(c)TBT composite (18.8 WPG) (d)TOT composite (17.4 WPG)
(e)TAA composite (15.4 WPG) (f)TAT composite (24.3 WPG)

2.3.2 Dimensional stability of various wood-inorganic composites

As shown in Table 2-1, TiO_2 wood-inorganic composites with higher bulking coefficient were found to show the higher ASE, and the composites with the higher ASE are prepared from the reagent with the lower rate in hydrolysis. Since such composites have inorganic gel formed within the cell walls, the topochemical effect must exist in these TiO_2 composites on their property enhancement, as seen in SiO_2 composites (Ogiso and Saka 1993). However, the values of ASE in these composites are not so high. To achieve even higher dimensional stabilization, a chemical bond of TiO_2 gel with cell wall components must be needed, as previously described (Saka and Yakake 1993, Ogiso and Saka 1994).

2.3.3 Thermal properties of various TiO_2 wood-inorganic composites

The results of TGA for these prepared wood-inorganic composites are

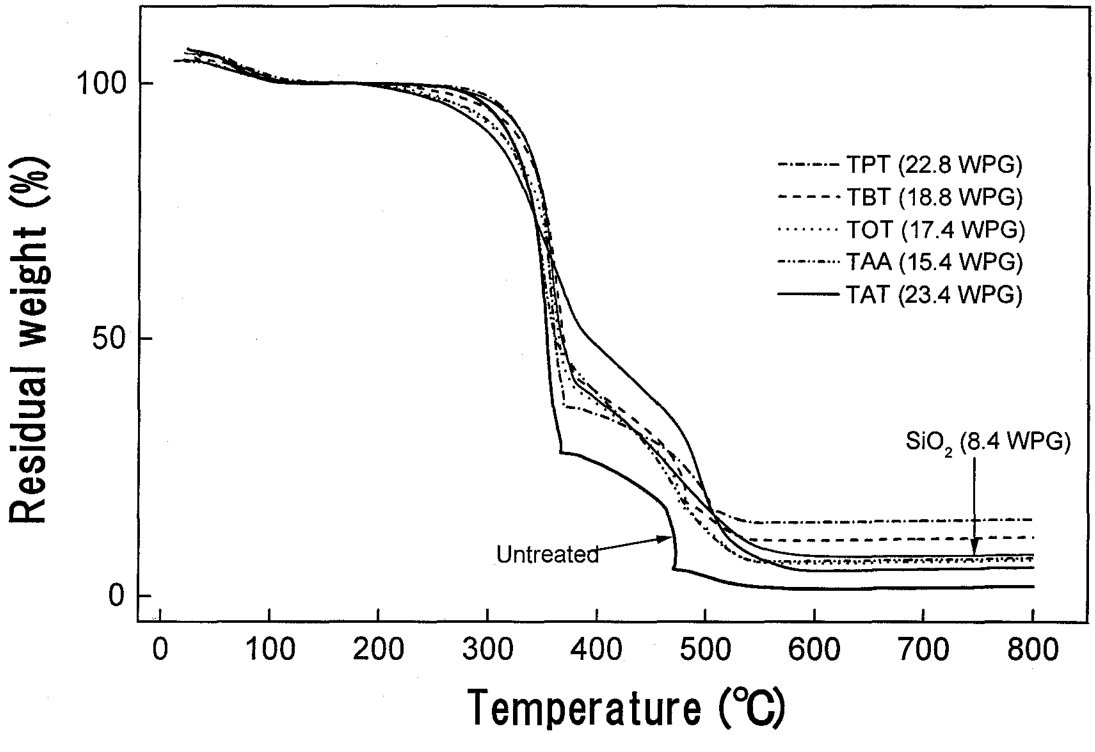


Fig. 2-3. TG curves for various TiO_2 wood-inorganic composites.

shown in Fig. 2-3. Compared with untreated wood, TPT composite is similar in its TG curve but all other composites show the higher residues after flaming at 370 ℃ with gradual decrease in their weights. TAT composites are especially high in its residue and more gradually decreased in their weight.

To understand the thermal properties of these composites furthermore, DTA was made and the obtained DTA curves are shown in Fig. 2-4. In the untreated wood, the first endothermic peak at about 340 ℃ is due to a pyrolysis of wood, and subsequent two exothermic peaks are due to flaming at 370 ℃ and glowing at 440 ℃. These characteristic peaks are very similar in TPT composite, but exothermic peak at a higher temperature is shifted 40 ℃ to the upper, compared with untreated wood. Since TPT composites have TiO_2 gel only in the cell lumens, the observed change in the DTA curve would be due to the effect of the lumen gel.

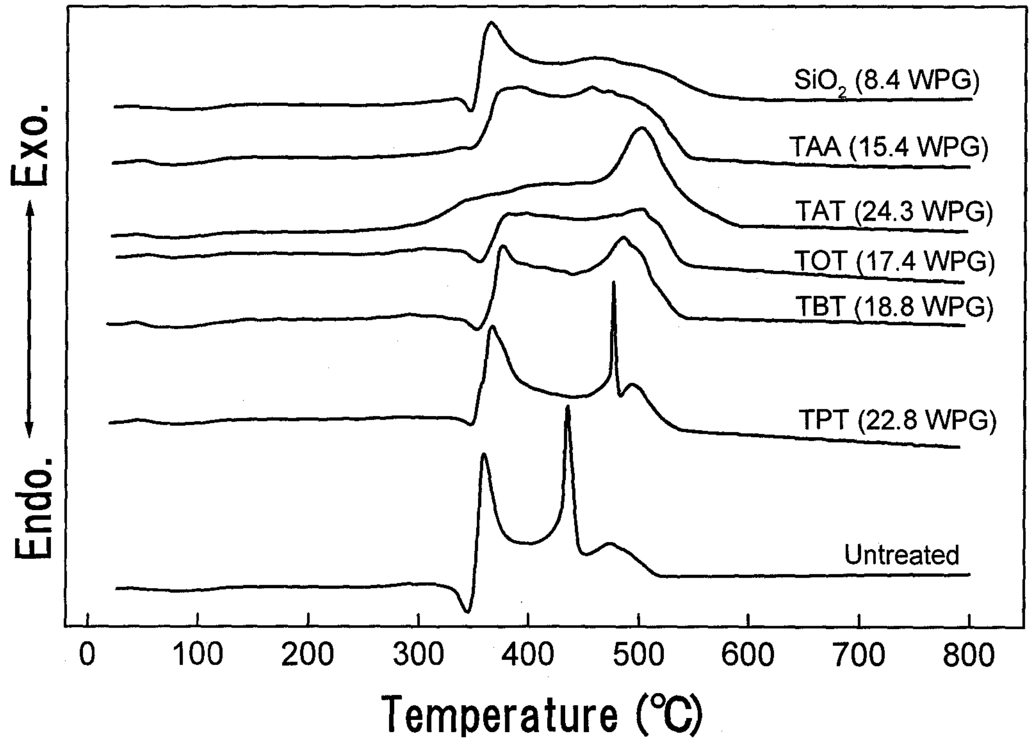


Fig. 2-4. DTA curves for various TiO_2 wood-inorganic composites.

In other TiO_2 composites, however, these characteristic peaks are weakened due to the inorganic modification of wood. Particularly, in TAT composites, the exothermic peak for flaming is disappeared in its DTA curve. As shown in Table 2-1, these composites are all having TiO_2 gel in the cell walls so that the difference in DTA curve, compared with untreated wood, would be due to inorganic modification of wood cell walls. It is quite apparent that the inorganic modification of wood cell walls is much more effective for the property enhancement than that of the cell lumens, in TiO_2 wood-inorganic composites.

As shown in Fig. 2-4, the DTA curves of these TiO_2 composites are similar to that of SiO_2 composites. As in a previous paper (Miyafuji and Saka 1996), SiO_2 gel is assumed to act as a chemical that melts and coats the cell wall components with a glassy layer with an elevation of temperature. This can prevent the cell wall components from escaping as volatile combustion products and from being accessible to oxygen. A similar mechanism must be applied to a TiO_2 gel deposited within the cell walls in all these composites.

However, among composites from TAA, TAT, TOT and TBT, TAT composites must be different in the fire-resisting mechanism, since they have the TiO_2 gel with the organic moieties of triethanolamine residues. Thus, mass chromatograms of 28 in m/z for TAT composites and untreated wood were obtained by the thermogravimetric analyzer coupled with the mass spectrometer (TG/MS), as shown in Fig. 2-5. The mass chromatogram (m/z 28) from the untreated wood is such that TAT composites must evolve mostly nitrogen gas in a temperature range between 350 and 420 ℃ from triethanolamine residues in the organic moieties. The evolved gas could dilute combustible volatiles to prevent wood from flaming. Therefore, as in DTA curve, TAT composites would have shown the higher fire-resistance for flaming. However, the effect of the inert gas generated would not be maintained enough over the temperature of 470 ℃, thus resulting in the observed exothermic peak for glowing.

As a conclusion, TiO_2 gel formed in the cell walls is effective for fire-resistance, as observed in SiO_2 composites previously (Ogiso and Saka 1993), and the topochemical effects of the TiO_2 gel exist for property enhancement of wood. This further indicates that without forming and distributing gel appropriately in wood, the maximal effects of the gel cannot be withdrawn for the enhancement of wood properties.

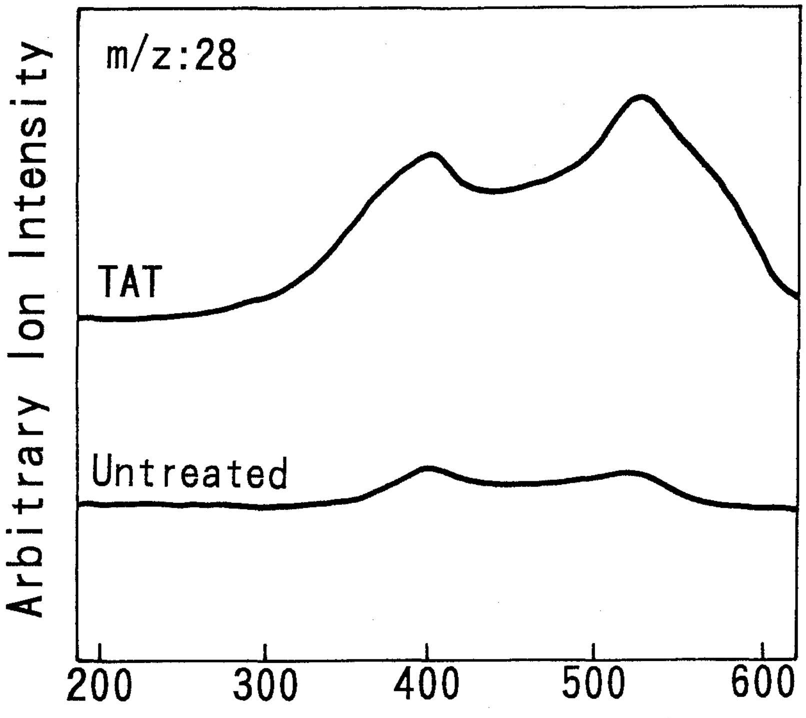


Fig. 2-5. Mass chromatograms of TAT composites and untreated wood as determined by the thermogravimetric analyzer coupled with mass spectrometer (TG/MS).

2.4 SUMMARY

Titanium alkoxides or titanium chelates which have the lower rate of hydrolysis and subsequent polycondensation than TPT were used for preparing TiO_2 wood-inorganic composites to study the topochemical effects of the TiO_2 gel for the property enhancement of wood. As a result, it was found by SEM-EDXA analysis that the TiO_2 gel formed within the cell walls could improve the properties of wood in dimensional stability and fire-resistance, whereas for the gel in the cell lumens, property enhancement could not be achieved, as observed in SiO_2 wood-inorganic composites.

Chapter 3

SiO_2-P_2O_5-B_2O_3 Wood-Inorganic Composites from Metal Alkoxides

3.1 INTRODUCTION

In Chapter 1, the wood-inorganic composites from various metal alkoxides in mono-reaction system were studied by thermogravimetric (TG) analysis and differential thermal analysis (DTA). From these results, it was found that the SiO_2, P_2O_5, and B_2O_3 composites could improve the thermal properties of wood, and have a good fire-resistance with a small WPG.

In this chapter, to enhance the properties of wood furthermore, the author has applied trimethylphosphite (TMP) or/and trimethylborate (TMB) to a reaction system of tetraethoxysilane (TEOS)/ethanol (EtOH)/acetic acid for preparing binary SiO_2-P_2O_5, SiO_2-B_2O_3 and ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites as mentioned in Chapter 1. For various composites prepared, the author studied their thermal properties by thermal analyses, and the effects of the P_2O_5 and B_2O_3 gels were evaluated on property enhancement of the SiO_2 wood-inorganic composites.

3.2 MATERIALS AND METHODS

3.2.1 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 (24 h) and water (24 h) in a Soxhlet apparatus. Extracted wood specimens were then oven-dried, and their oven-dried weights were measured. The unextracted specimens [120 (R) × 1 (T) × 120 (L) mm] of western red cedar (*Thuja plicata* D.Don) were also used in this study for plywood preparation. To prepare the moisture-conditioned wood specimens with 20 to 25% moisture contents, oven-dried specimens were placed in a desiccator for three weeks at 20 ℃ in which the relative humidity was controlled to be 98% by a saturated salt solution of K_2SO_4.

3.2.2 Preparation of wood-inorganic composites

A solution with a molar ratio of 1:1:0.01 in TEOS, EtOH, and acetic acid was prepared for SiO_2 wood-inorganic composites. To this solution, TMP or/and TMB was/were added to prepare binary SiO_2-P_2O_5 composites, SiO_2-B_2O_3 composites, or ternary SiO_2-P_2O_5-B_2O_3 composites. To prepare several kinds of SiO_2-P_2O_5 composites and SiO_2-B_2O_3composites, different molar ratios of TMP or TMB to TEOS were made: 0.01, 0.05, 0.1, and 0.5, as in Table 3-1. Just for comparison, P_2O_5 composites and B_2O_3 composites were also prepared with a solution of TMP or TMB in ethanol with acetic acid (molar ratio, 1:1:0.01), without TEOS.

Into moisture-conditioned specimens, the prepared solutions were impregnated at 20 ℃ under a reduced pressure (15 mmHg) for three days. The impregnated specimens were then placed in an oven controlled to be 65 ℃ for 24 h and 105 ℃ for another 24 h for aging of the gel.

3.2.3 Evaluation of wood-inorganic composites

The weight percent gain (WPG) of the composites was determined by the same procedure described in Chapter 1. From the obtained WPGs, the contents of the inorganic substances in the composites were computed.

The contents of the SiO_2 and P_2O_5 gels were also determined individually from Si and P weight concentrations by a JEOL scanning electron microscope (JSM-T330A) coupled with an EDAX 9100/70 energy dispersive X-ray spectrometer (SEM-EDXA) at 20 kV. The contents of B_2O_3 gel could not be determined due to the inability of boron determination by the SEM-EDXA system.

The antiswelling efficiency (ASE) was determined by the same procedure

Table 3-1. Inorganic substances in various wood-inorganic composites.

Wood composites	Molar ratios			WPGs (%)	Contents of inorganic substances (wt%)					
	TEOS	TMP	TMB		Weight determinations	TG[a]	EDXA			
							Totals	SiO_2	P_2O_5	B_2O_3
SiO_2	1	0	0	8.3	7.7	8	9.3	9.3	0	0
SiO_2-P_2O_5	1	0.01	0	10.7	9.7	11	14.3	10.5	3.8	0
	1	0.05	0	22.4	18.3	18	26.0	15.6	10.4	0
	1	0.1	0	17.1	14.6	20	20.4	11.0	9.4	0
	1	0.5	0	7.5	7.0	10	13.1	1.1	12.0	0
SiO_2-B_2O_3	1	0	0.01	5.3	5.0	7	ND	4.7	0	ND
	1	0	0.05	17.3	14.7	17	ND	18.3	0	ND
	1	0	0.1	32.4	24.5	25	ND	28.7	0	ND
	1	0	0.5	37.2	27.1	25	ND	32.7	0	ND
SiO_2-P_2O_5-B_2O_3	1	0.1	0.1	34.3	25.5	28	ND	30.2	9	ND
P_2O_5	0	1	0	9.4	8.6	18	14.8	0	14.8	0
B_2O_3	0	0	1	9.9	9.0	16	ND	0	0	ND

[a] Residual content at 800 ℃ after the TG analysis. ND: not determined.

described in Chapter 2.

For testing thermal properties, about 8-10 mg of composite specimen were studied with a thermogravimetric analyzer, Shimadzu TGA-50, and a differential thermal analyzer, Shimadzu DTA-50, with a flow of dried air (50 ml/min), unless otherwise indicated. The temperature was raised from 20 to 800 ℃ at a heating rate of 20 ℃/min. To evaluate a degradation of the specimen, the temperature at which one-tenth of the original wood weight was lost was determined from the obtained thermogram, assuming that a specimen at 170 ℃ had no loss of weight. From the thermogram, the residual content at the temperature of 800 ℃ was also determined.

Five-plywood [120 × 12 × 5 mm] was also prepared for all composites. A pair of treated and untreated specimens were set together to be in a V-shape at an angle of 30° over the horizontal line. These specimens were then burned together at the tip of the V-shape with a gas burner for 30 s. After 30 s, the gas burner was removed, and the specimens were kept burning until they disappeared. The gas burner was controlled carefully to be constant during the entire course of all tests. Each carbonized composite specimen after burning was then surfaced with a razor knife, and the exposed transverse surface was studied with a JOEL scanning electron microscope (JSM-T330A) at 20 kV for its morphology and distribution of SiO_2 and P_2O_5 gels in the composite.

3.3 RESULTS AND DISCUSSION

3.3.1 The content of inorganic substances

Table 3-1 shows the contents of inorganic substances in various wood-inorganic composites. As a measure of the inorganic substances in the wood-inorganic composites, the WPGs were obtained as in Table 3-1. Because the WPGs are weight percent gains over 100% of wood, the contents of inorganic substances are also shown, computed from the WPGs, the thermogravimetric (TG) determinations at 800 ℃, and SEM-EDXA measurements of the Si and P concentrations in the composites. Due to the inability to measure boron by the EDXA system, the content of B_2O_3 gel could not be determined. Thus, the total content of inorganic substances in some composites with B_2O_3 gel could not be determined.

Comparisons of these results from three different determinations in Table 3-1 can indicate that all these basically agree well with each other. However, a closer inspection suggests some differences. The results by the TG determinations are based on the complete ashing of wood components and polycondensation of the inorganic substances during a process rising from an ambient temperature to 800 ℃. Therefore, inorganic substances subjected to the TG determination are somewhat different in structure from those of the wood-inorganic composites treated during the sol-gel process at the temperatures of 65 and 105 ℃. Such a difference must be reflected in the results.

The inorganic substances studied by EDXA determination are therefore those of the latter. However, the contents of the inorganic substances computed from the WPGs were generally less than those determined by EDXA measurements. Because the reaction media for the binary and ternary systems were somewhat acidic, the wood cell wall components of the composites might have been extracted to some extent during the preparation of the composites. This would have resulted in underestimations of the results of their contents from the WPGs.

In SiO_2-P_2O_5 composites, the total content of the SiO_2-P_2O_5 was found to be maximal with the molar ratio of TEOS/TMP being 1/0.05. This is due to the content of SiO_2 gel which is also maximal in the molar ratio of 1/0.05. The content of the P_2O_5 gel, on the other hand, was rather constant in the ratio of 1/0.05, 1/0.1, and 1/0.5. In SiO_2-B_2O_3 composites, with an increasing molar ratio of TMB to TEOS, the content of SiO_2 gel was increased.

3.3.2 Distribution of the inorganic substances

Figure 3-1 shows the SEM micrographs (left) and EDXA spectra (right) obtained by point analyses of the cell wall for various wood-inorganic composites. Due to inability of the boron measurements by EDXA system, boron peak could not be obtained for SiO_2-B_2O_3 composites and SiO_2-P_2O_5-B_2O_3 composites. In SiO_2 wood-inorganic composite and binary SiO_2-P_2O_5 wood-inorganic composite, the inorganic substances were not observed in cell lumens. However, as shown in the EDXA spectra of the cell wall, Si-Kα and P-Kα X-rays were detected. Therefore, the SiO_2 and P_2O_5 gels must be distributed only within the cell walls. On the other hand, in binary SiO_2-B_2O_3 wood-inorganic composites and ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composite which have high WPGs over 30%, the inorganic substances were found to be deposited in cell lumens as well as cell walls by SEM-EDXA analysis.

3.3.3 Dimensional stability of various wood-inorganic composites

Figure 3-2 shows the relationships between WPGs and ASEs in various wood-inorganic composites. Just for comparison, the previous results (Saka *et al.* 1992a) of the SiO_2 composites in which the SiO_2 gel is formed within the cell walls are also plotted in the figure. It is apparent that as the WPGs of the composites increase up to about 10%, the ASEs increase effectively. However, above 10% in WPG, the ASE only increases gradually, but the SiO_2-P_2O_5 composites seem to have the larger ASEs with the same WPGs, compared with the SiO_2-B_2O_3 composites.

The SEM-EDXA observations have revealed that as the WPGs increase over 10%, P_2O_5 or/and B_2O_3 gels started being deposited in the cell lumens in addition to the cell walls. This would be the reason why the ASE did not

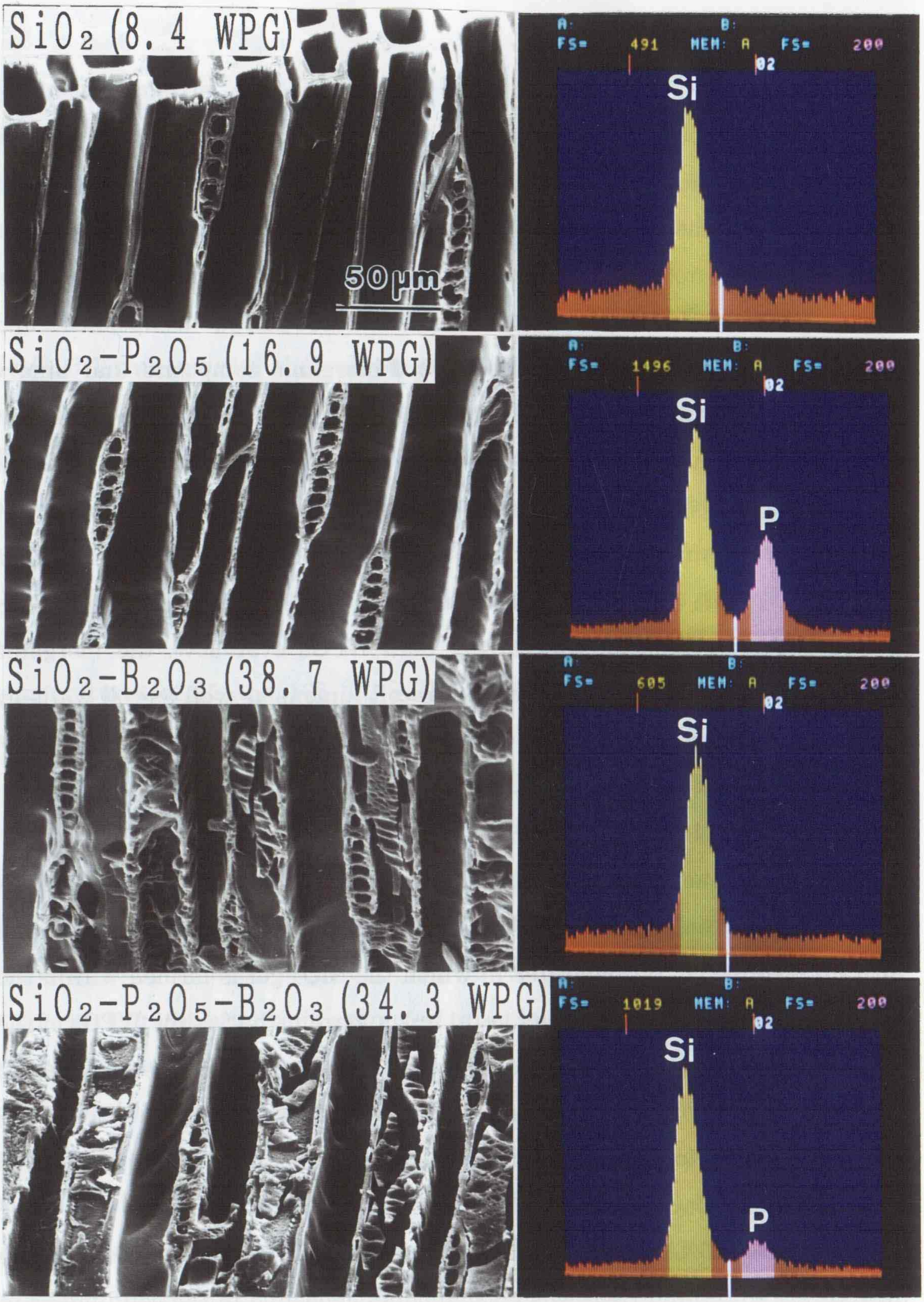


Fig. 3-1. Comparisons in various wood-inorganic composites.
(left: SEM micrographs, right: EDXA spectra of Si-Kα and P-Kα X-rays)

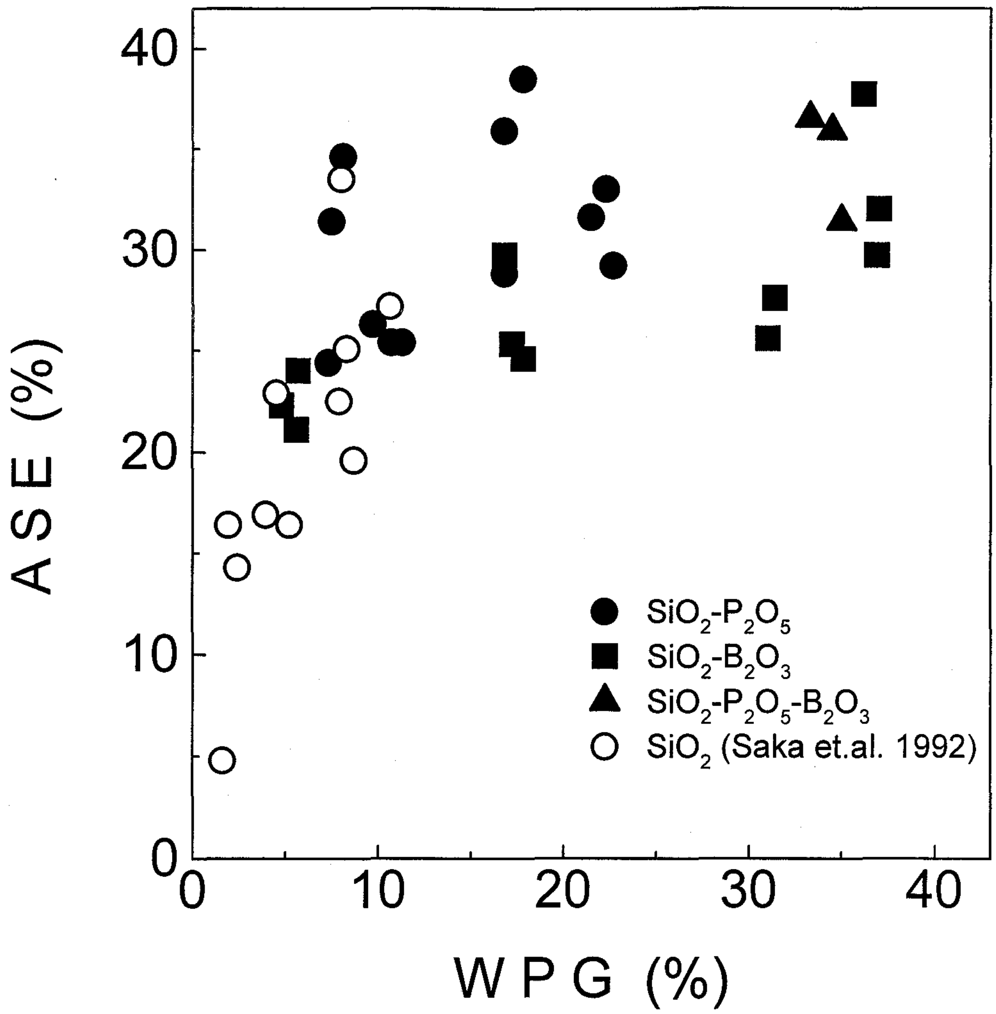


Fig. 3-2. Relationship between WPGs and ASEs in various wood-inorganic composites.

increase as the WPG increased.

3.3.4 Fire-resistance in various wood-inorganic composites

3.3.4.1 TG and DTA analyses

Figure 3-3 shows the TG curves of various SiO_2-P_2O_5 wood-inorganic composites, compared with untreated wood and SiO_2 wood-inorganic composites. It should be noted that the TG curves of SiO_2-P_2O_5 composites during the flaming shifted to the lower temperature with increasing the TMP

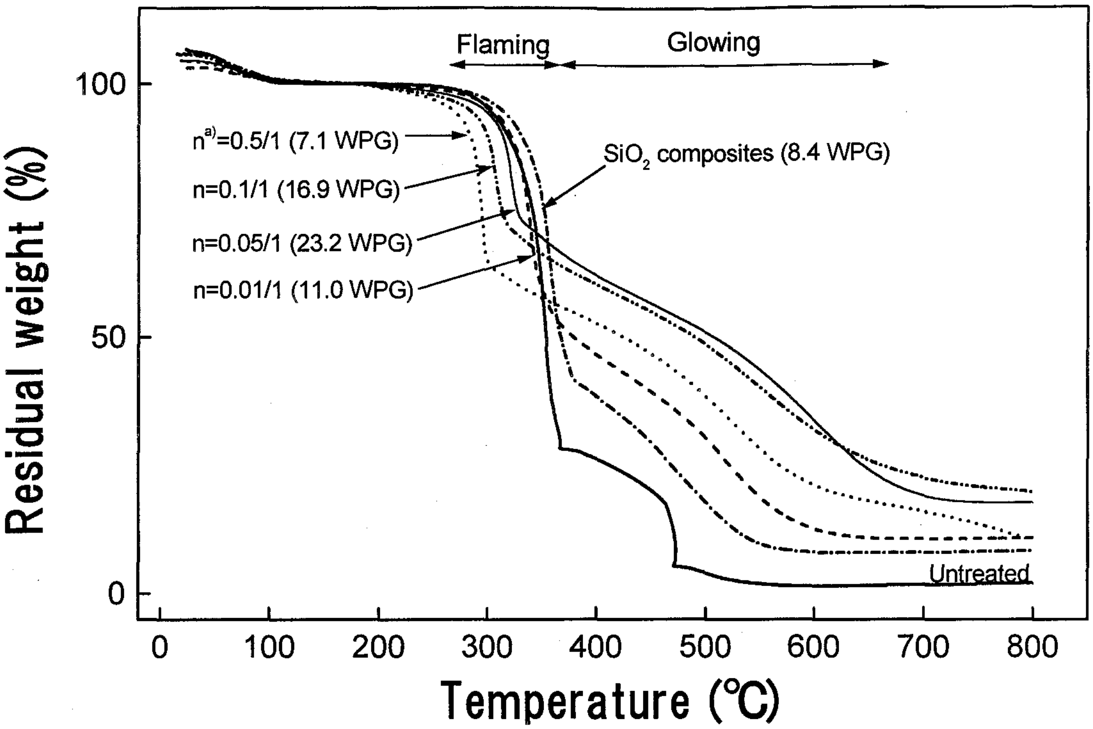


Fig. 3-3. TG curves for various SiO_2-P_2O_5 composites.
a)n=TMP/TEOS in molar ratio

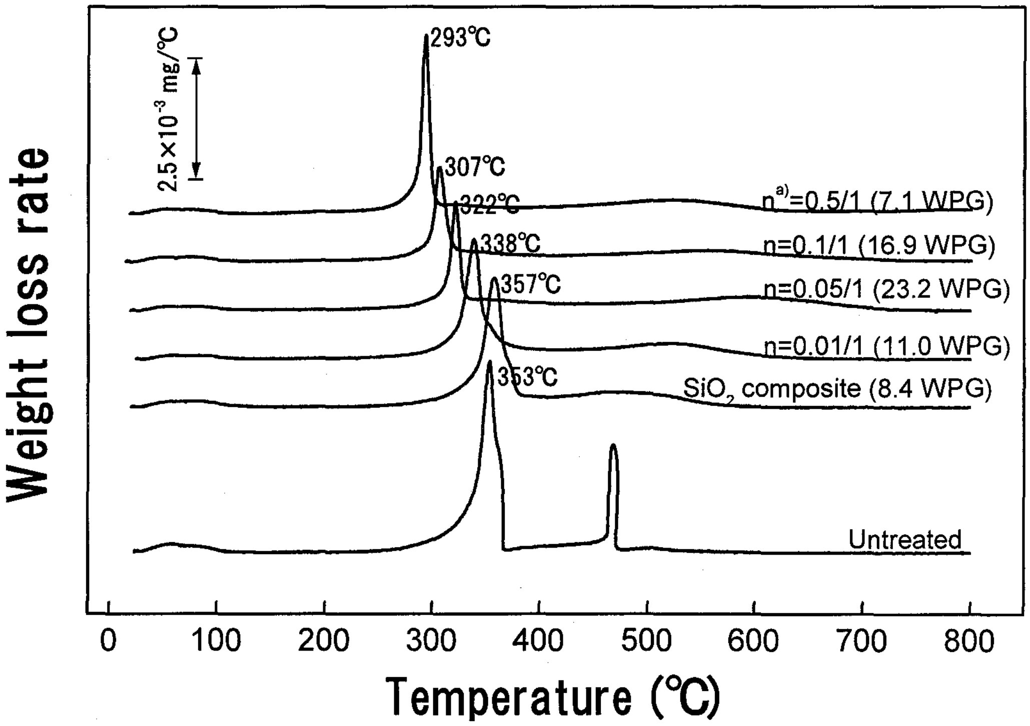


Fig. 3-4. DTG curves for various SiO_2-P_2O_5 composites.
a)n=TMP/TEOS in molar ratio

addition to reaction mediums. Such a shift is obviously noted in the peak temperature of derivative thermogravimetric (DTG) curves for the flaming as in Fig. 3-4. In addition to this, the TG curves of SiO_2-P_2O_5 wood-inorganic composites show the higher residue after flaming with the gradual decrease during glowing, compared with untreated wood or SiO_2 wood-inorganic composites.

The DTA curves of various SiO_2-P_2O_5 wood-inorganic composites are also shown in Fig. 3-5. In the SiO_2-P_2O_5 composites, no apparent exothermic peaks are observed during flaming or glowing. Instead, a very broad exothermic hill is continued up to over 600 ℃. These results of TG and DTA indicated a strong resistance of the composites against the thermal attack and a striking effect of P_2O_5 gel on the fire-resistance.

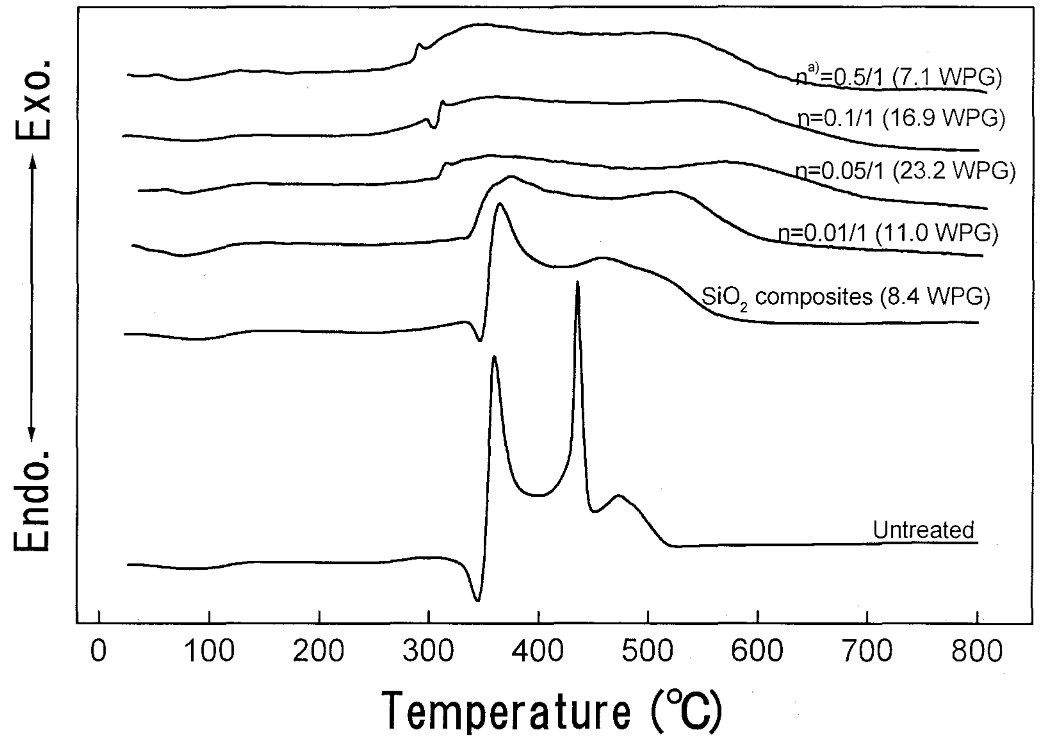


Fig. 3-5. DTA curves for various SiO_2-P_2O_5 composites.
[a)]n=TMP/TEOS in molar ratio

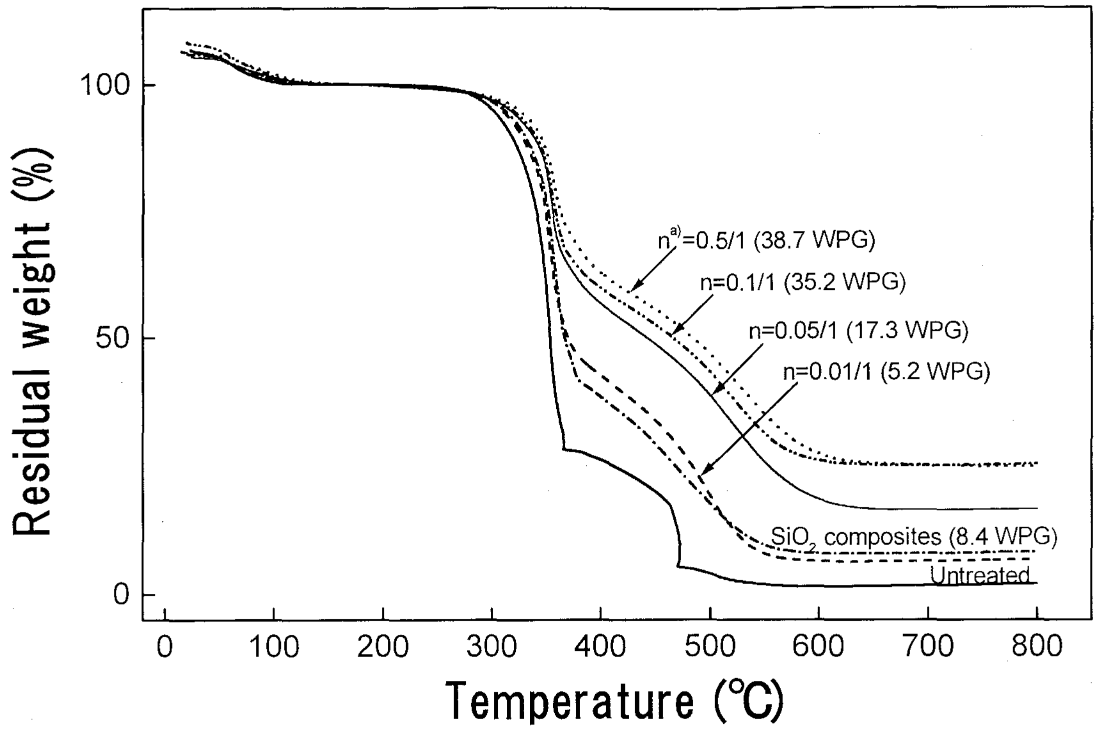


Fig. 3-6. TG curves for various SiO_2-B_2O_3 composites.
[a)]n=TMB/TEOS in molar ratio

Figure 3-6 shows the TG curves of various SiO_2-B_2O_3 wood-inorganic composites, compared with untreated wood and SiO_2 wood-inorganic composites. It should be noted that the TG curve of SiO_2-B_2O_3 wood-inorganic composites during the flaming shifted to the upper temperature with increasing the TMB addition to reaction mediums. Nevertheless, this shift can not be seen clearly in the peak temperature of DTG curves during flaming as shown in Fig. 3-7. Again in the TG curves of various SiO_2-B_2O_3 wood-inorganic composites, these TG curves shows the higher residue after flaming with the gradual decrease during glowing, compared with untreated wood or SiO_2 wood-inorganic composites.

The DTA curves of various SiO_2-B_2O_3 wood-inorganic composites are also shown in Fig. 3-8. In SiO_2-B_2O_3 wood-inorganic composites in a molar ratio of TMB/TEOS being 0.01/1, 0.05/1, and 0.1/1, an exothermic peak was

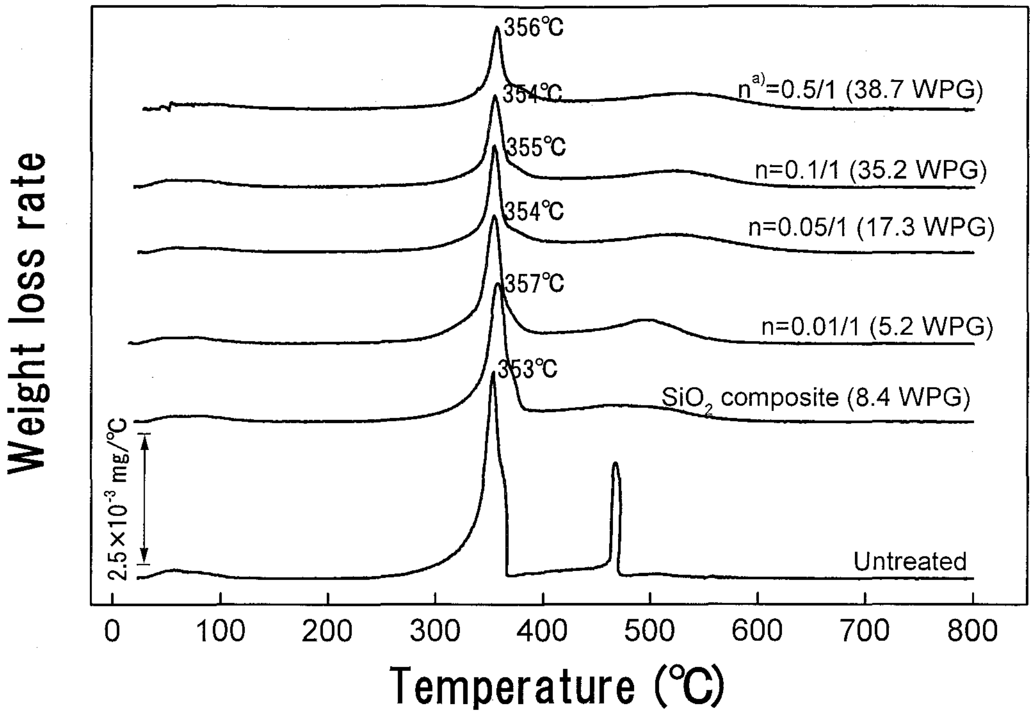


Fig. 3-7. DTG curves for various SiO_2-B_2O_3 composites.
[a]n=TMB/TEOS in molar ratio

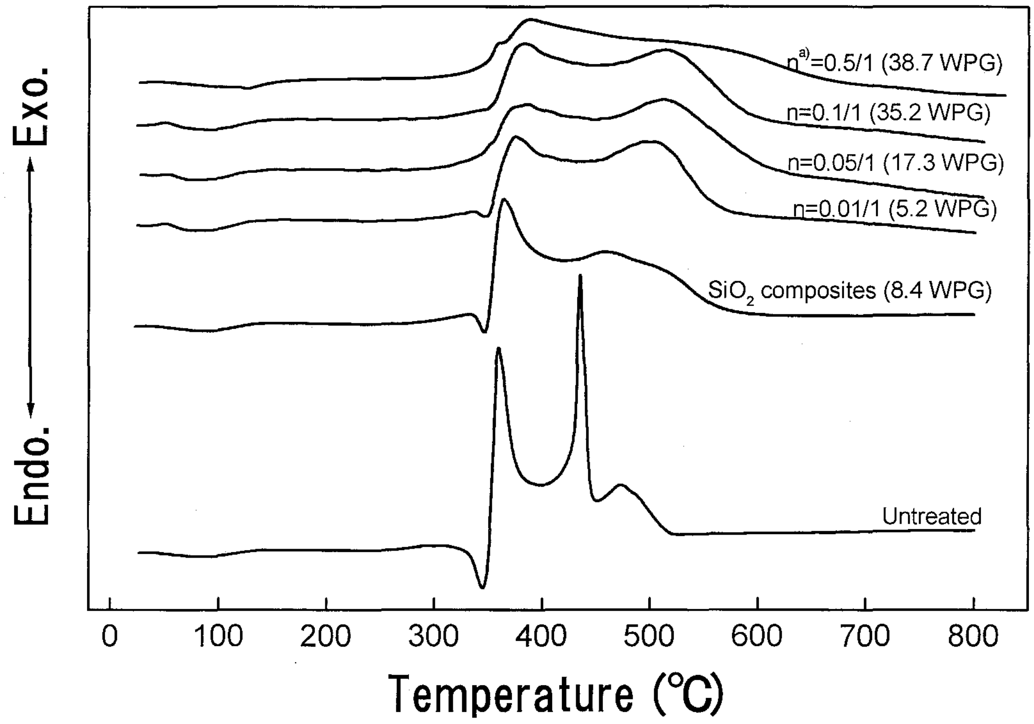


Fig. 3-8. DTA curves for various SiO_2-B_2O_3 composites.
[a]n=TMB/TEOS in molar ratio

weakened and broadened, compared with untreated wood or SiO_2 wood-inorganic composites. Furthermore, in SiO_2-B_2O_3 wood-inorganic composites in a molar ratio of TMB/TEOS being 0.5/1, an exothermic peak has disappeared and one broad exothermic curve was continued up to about 600℃. From these results, SiO_2-B_2O_3 wood-inorganic composites must have an enhanced fire-resistance. However, compared with results of TG and DTA in SiO_2-P_2O_5 wood-inorganic composites, fire-resisting effect of SiO_2-B_2O_3 wood-inorganic composites seems to be slightly inferior.

Figure 3-9 shows the TG curves of ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites, compared with untreated wood, SiO_2, SiO_2-P_2O_5, and SiO_2-B_2O_3 wood-inorganic composites. The TG curve of ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites was found to be similar to that of SiO_2-P_2O_5wood-inorganic composites. That is, these composites show the first abrupt decrease in weight to the lower temperature with the higher residue after flaming with the gradual decrease during glowing.

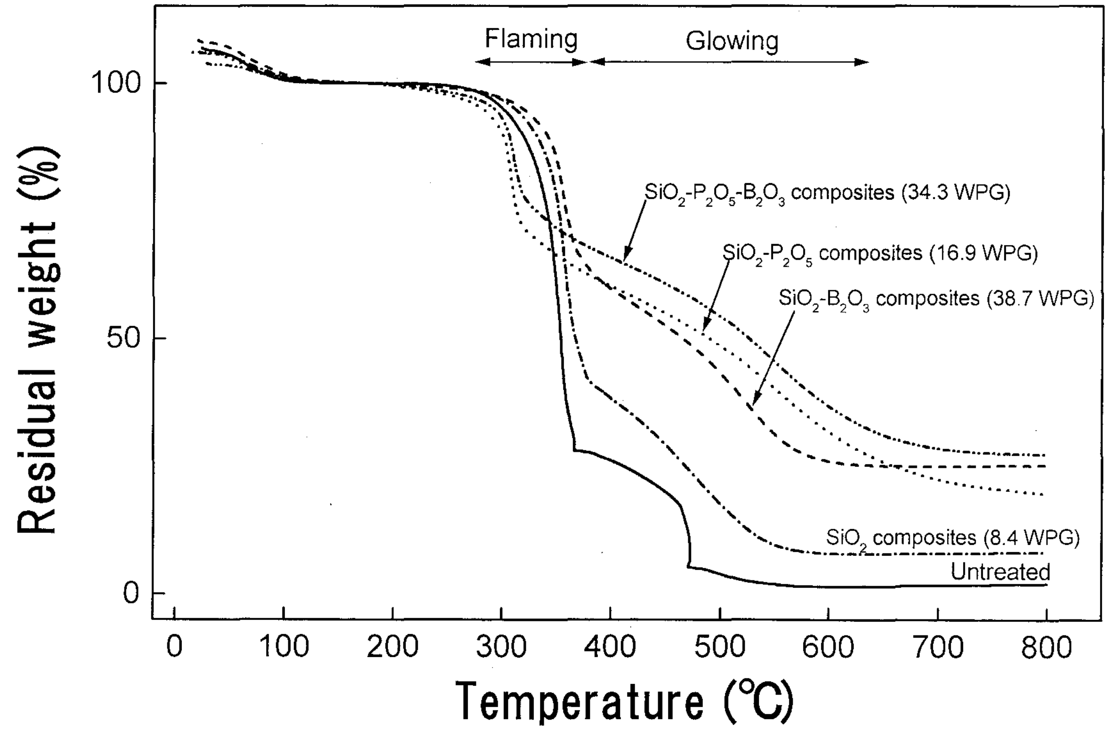


Fig. 3-9. TG curves for various wood-inorganic composites.

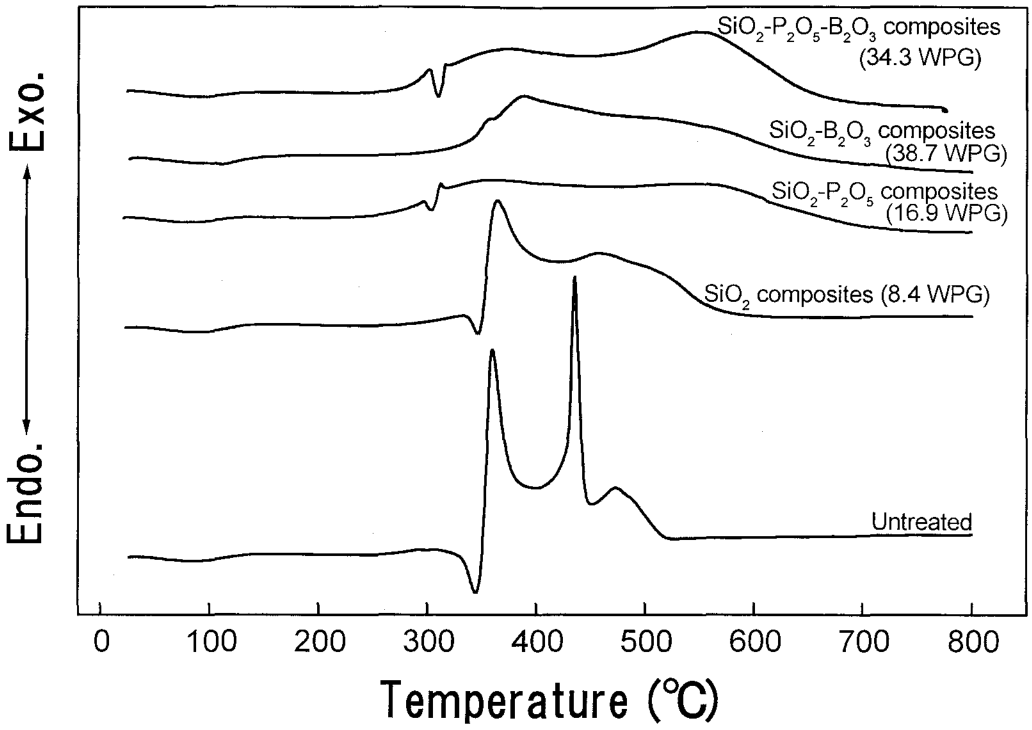


Fig. 3-10. DTA curves for various wood-inorganic composites.

The DTA curves of ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites are also shown in Fig. 3-10. As similar to SiO_2-P_2O_5 or SiO_2-B_2O_3 wood-inorganic composites, no apparent exothermic peaks can be seen, but some broad exothermic peak is present. This indicates that this ternary composites are most fire-resistant.

A previous work indicated a specificity of B_2O_3 gel for its formation in the cell walls (Saka and Kitazawa 1993). Thus, the B_2O_3 gel must also be formed within cell walls in this study. Furthermore, the EDXA study in the carbonized cell walls revealed the presence of Si and P for the SiO_2-P_2O_5 and SiO_2-P_2O_5-B_2O_3 composites. Therefore, compared with the SiO_2 composites, improved fire-resisting effects in the binary and ternary systems of composites are due to the P_2O_5 or/and B_2O_3 gels deposited within the cell walls of the composites.

Overall results from TG and DTA analyses clearly indicated that in binary and ternary systems, flaming and subsequent glowing are both restrained. These results have revealed the SiO_2-P_2O_5-B_2O_3 wood-inorganic composites are much superior in fire-resistance to untreated wood or SiO_2 wood-inorganic composites. As a next trial, five plywoods were prepared from various wood-inorganic composites for practical applications and fire-resistance test for them was made to ensure their fire-resisting effect.

3.3.4.2 Fire-resistance test

Figure 3-11 shows the comparisons between some plywood specimens from untreated wood and various wood-inorganic composites. The plywoods from various wood-inorganic composites could not be distinguished from untreated plywood by their appearances, because the inorganic substances mainly distributed within the cell wall. Figure 3-12 shows the fire-resistance test of various wood-inorganic composites (right), compared with untreated plywood (left). Figure 3-13 shows comparisons of the burned specimen after fire-resistance test. Although untreated plywood specimens were all burned, the SiO_2 composites were found to show some fire-resistance. Furthermore, SiO_2-P_2O_5, SiO_2-B_2O_3 and SiO_2-P_2O_5-B_2O_3 composites revealed all much higher resistance against burning.

Figure 3-14 shows the SEM micrographs of these carbonized composites after this burning test. The burned wood specimen (a) shows very thin residual cell walls as previously reported (Ogiso and Saka 1993). However, the SiO_2-P_2O_5, SiO_2-B_2O_3 and SiO_2-P_2O_5-B_2O_3 composites (c, d and e, respectively) revealed very thick cell walls and they are even thicker than those of the SiO_2 composites (b). Such differences in the morphology of the carbonized composites are due presumably to the very high residual weights observed in the TG curves, just after flaming. These results of the fire-resistance test and SEM observations ensured the fire-resistance shown by results of TG and DTA analyses.

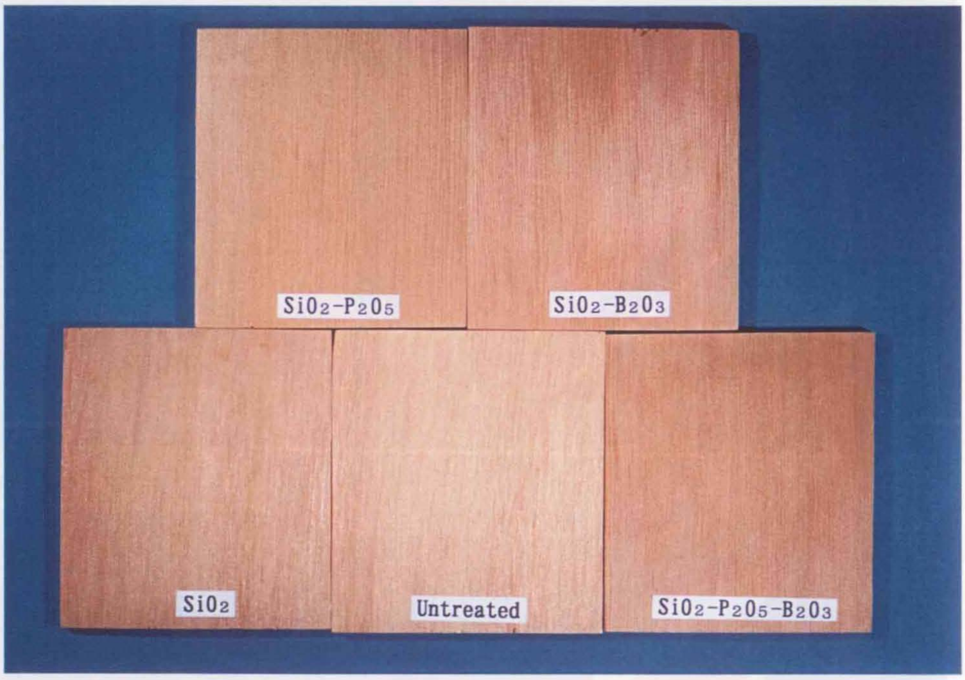


Fig. 3-11. Comparisons between untreated plywood specimens and various wood-inorganic composites.

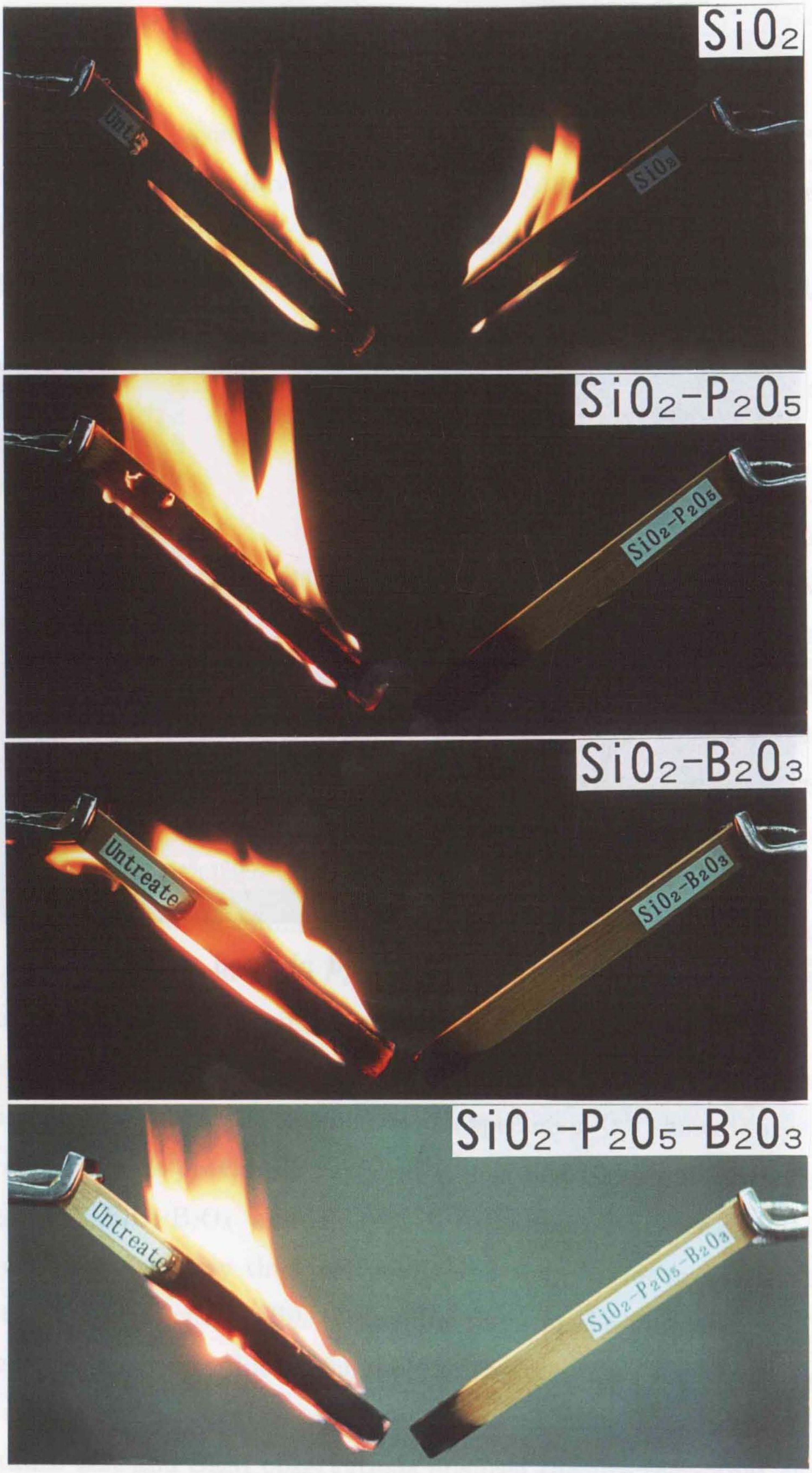


Fig. 3-12. Comparisons of fire-resisting properties in various wood-inorganic composites by fire-resistance test.
(left:untreated specimen, right:various wood-inorganic composites)

Fig. 3-13. Comparisons of the burned specimens after the fire-resistance test. Untreated plywood specimens (left) *vs.* various wood-inorganic composites (right).

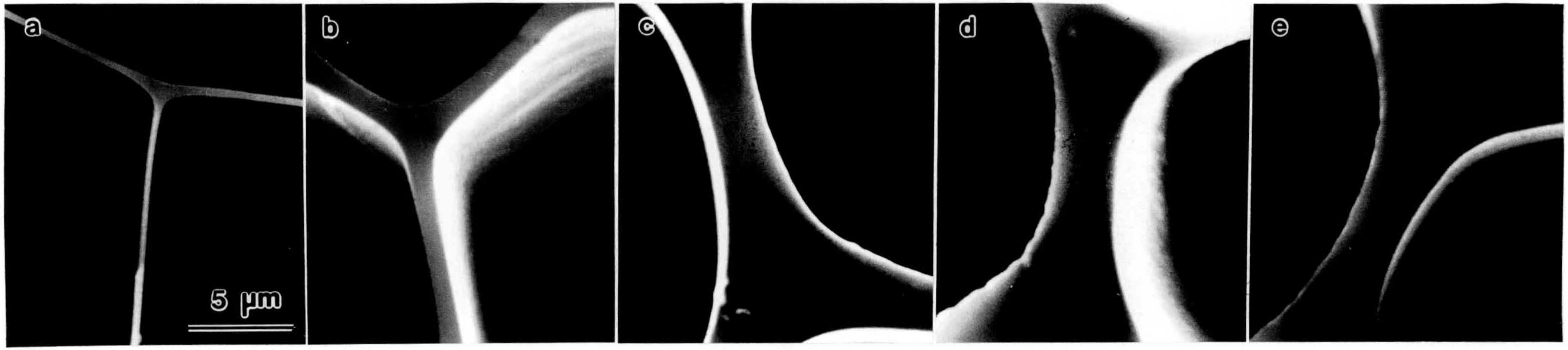


Fig.3-14. Comparisons of carbonized wood-inorganic composites after burning.
(a) Untreated specimen (b) SiO_2 composite (9.5 WPG) (c) SiO_2-P_2O_5 composite (16.9 WPG)
(d) SiO_2-B_2O_3 composite (38.7 WPG) (e) SiO_2-P_2O_5-B_2O_3 composite (34.3 WPG).

3.3.5 Mechanisms of fire-resistance of various wood-inorganic composites

To clarify the mechanisms of fire-resistance of wood-inorganic composites, TG analyses were made with a flow of dried air or dried nitrogen.

Prior to this evaluation, SiO_2, P_2O_5, and B_2O_3 gels were individually studied by these TG analyses, and these gels were found to be fairly stable with only small percentage losses of their weights at a temperature range between 170 ℃ and 350 ℃.

To evaluate the fire-resisting effects among different wood-inorganic composites, comparisons must be made at the same level of wood degradation. Fortunately, the gel in composites was so stable in a temperature range above (170-350 ℃), that the losses of the composites are due to those of the cell wall components. Therefore, the author has compared the thermal degradation temperature ($T_{d10\%}$) at which one-tenth of the original wood weight was lost. By this way, direct comparisons could be made on the fire-resisting effects of wood-inorganic composites.

The thermal degradation temperature ($T_{d10\%}$) defined above was determined from the obtained TG curve as the percentage of the residual weight of the wood-inorganic composite calculated by equation (3-1).

$$\frac{90 + a}{100 + a} \times 100\ (\%) \qquad (3\text{-}1)$$

where "a" is the WPG of the composite.

The obtained $T_{d10\%}$ is shown in Table 3-2. The TG analysis with a flow of air indicated that in both SiO_2 and B_2O_3 composites, its temperature rose to 328 and 334 ℃, respectively from 320 ℃ of the untreated specimens. Similarly, $T_{d10\%}$ of the SiO_2-B_2O_3 composites rose also. However, in P_2O_5 composites, the temperature was lowered to 271 ℃ from 320 ℃ of the untreated specimens. In a similar manner, all specimens of SiO_2-P_2O_5 composites and SiO_2-P_2O_5-B_2O_3 composites were lowered in their temperatures.

Table 3-2. Comparisons of thermal degradation temperatures of air and nitrogen flows as determined by thermogravimetric analyses.

	Molar ratios			WPGs	$T_{d10\%}$(℃)[a)]	
Wood composites	TEOS	TMP	TMB	(%)	Air	Nitrogen
Untreated		–			320	335
SiO_2	1	0	0	8.3	328	345
SiO_2-P_2O_5	1	0.01	0	10.7	318	326
	1	0.05	0	22.4	309	313
	1	0.1	0	17.1	296	299
	1	0.5	0	7.5	282	284
SiO_2-B_2O_3	1	0	0.01	5.3	326	338
	1	0	0.05	17.3	333	346
	1	0	0.1	32.4	332	341
	1	0	0.5	37.2	336	348
SiO_2-P_2O_5-B_2O_3	1	0.1	0.1	34.3	301	306
P_2O_5	0	1	0	9.4	271	271
B_2O_3	0	0	1	9.9	334	340

[a)] Thermal degradation temperature at a loss of one-tenth of the original wood.

Such results suggest that the fire-resisting effects must be different between P_2O_5 gel and SiO_2 or B_2O_3 gel. According to the coating theory of Browne (1958), boric compound is believed to act as a chemical that melts and coats the cell wall components with a glassy layer with an elevation of temperature. This can prevent the cell wall components from escaping as volatile combustion products and being accessible to oxygen. This theory must be examined for its fire-resisting effect, but a similar mechanism could be applied to a silicic compound for the fire-resistance of wood. On the other hand, phosphorous compounds are known to encourage the pyrolysis of wood to carbon and water by their reactivity with wood hydroxyl groups and by the avidity with which they absorb water (Browne 1958). Such different mechanisms against fire-resisting effects would have resulted in shifting the temperature for flaming lower for P_2O_5 gel and higher for SiO_2 and B_2O_3 gels.

Upon the TG analysis with a flow of nitrogen, $T_{d10\%}$ generally rises, compared with that under a flow of air. However, P_2O_5 gel resulted in a very small rise (0-4 ℃) in temperature. Therefore, as indicated above, phosphorous compounds act chemically for the fire-resistance of wood, regardless of the presence of oxygen. On the other hand, a finding for SiO_2 and B_2O_3 gels that a lack of oxygen under a nitrogen flow results in a rise of $T_{d10\%}$, can support the physical effect of barriers with melted and coated gel on their fire-resistance. However, temperature rise for the $T_{d10\%}$ was larger for SiO_2 composites (17 ℃) than it was for B_2O_3 composites (6 ℃) or SiO_2-B_2O_3 composites (7-12 ℃). Because this temperature rise would be smaller in the case of the large physical effect of barriers, B_2O_3 gel would be better in fire-resisting ability than SiO_2 gel by its barrier effect.

3.4 SUMMARY

For enhancing the properties of wood furthermore, the binary SiO_2-P_2O_5, SiO_2-B_2O_3 and ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites were prepared in this chapter. The results of the thermal analyses on the obtained composites revealed their enhanced fire-resisting properties, compared with the untreated wood and SiO_2 composites. The fire-resisting effects of these binary and ternary wood-inorganic composites may be due to the physical effects of the SiO_2 and B_2O_3 gels, and chemical effects of the P_2O_5 gel.

Consequently, the ternary SiO_2-P_2O_5-B_2O_3 composites have all of these not only physical but also chemical effects on their fire-resistances. It must further be emphasized that these composites, with only at most 35% in WPGs, have excellent thermal properties, while keeping more or less the porous structure characteristics of wood.

Chapter 4

SiO_2-P_2O_5-B_2O_3 Wood-Inorganic Composites from Metal Alkoxide Oligomers

4.1 INTRODUCTION

In Chapter 3, the author has applied trimethylphosphite (TMP) and/or trimethylborate (TMB) to a reaction system of TEOS/EtOH/acetic acid to prepare binary SiO_2-P_2O_5, SiO_2-B_2O_3 and ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites. On these composites, the thermal properties were evaluated and these binary and ternary composites were found to have more enhanced fire-resisting properties than SiO_2 composites.

However, such composites with enhanced properties were found to have some problems in the stability of P_2O_5 and B_2O_3 gels against weathering. To overcome such problems, some property-enhancers were added to binary reaction system of TEOS/EtOH/acetic acid with TMP or TMB (Saka and Tanno 1996). The obtained composites were found to restrain the leaching of the gel and maintain the high fire-resisting properties after the leaching test.

In this chapter, to overcome the odor and harm problems of chemicals in TMP and TMB for environmental safety, the author has applied some silicon alkoxide oligomers with phosphorous and/or boric hydroxide residues to prepare the SiO_2-P_2O_5-B_2O_3 wood-inorganic composites and compared their thermal properties with composites from alkoxide monomers. Additionally the anti-leachability of the SiO_2-P_2O_5-B_2O_3 gels against the weathering were evaluated.

4.2 MATERIALS AND METHODS

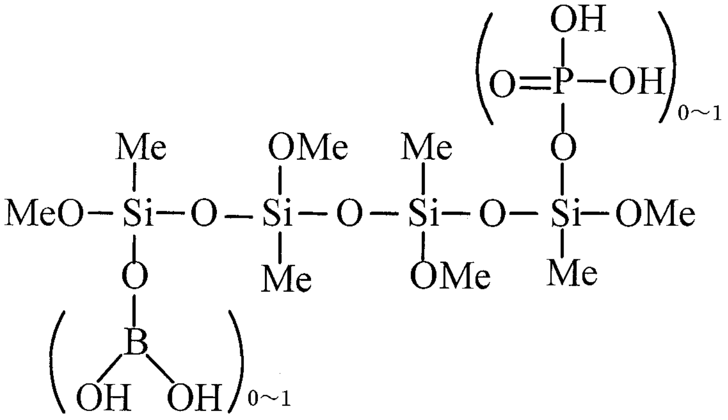
4.2.1 Wood specimens

The wood specimens were prepared by the same procedure described in Chapter 1.

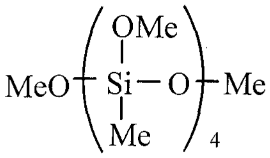
4.2.2 Wood-inorganic composites with metal alkoxide oligomers

Wood-inorganic composites were prepared in this study with metal alkoxide oligomers, and the oligomers were prepared by the following procedure :

As in Fig. 4-1, methylmethoxydisiloxane ; $H_3C(H_3CO)_2SiOSi(OCH_3)_2CH_3$ (Ag), methyltrimethoxysilane ; $CH_3Si(OCH_3)_3$ (Bg), and boric acid (Cg) were mixed with 35%HCl aqueous solution (0.02g) in designated amounts shown in Table 4-1, and then the mixture was stirred for 2 h at 30 ℃. Subsequently, 85%H_3PO_4 aqueous solution (Dg) was continuously dropped into this mixture for 30 min. The resulting solution was maintained at 65 ℃ for 1 h for ripening. The ripened solution was then filtrated for metal alkoxide oligomer reagents. The prepared oligomers were thought to have a structure as described below.



However, these oligomers were assumed to be



$$\mathrm{MeO}\left(\overset{\mathrm{OMe}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}\right)_4\mathrm{Me}$$

(molecular weight: 406) in structure with phosphorous and/or boric hydroxide residues.

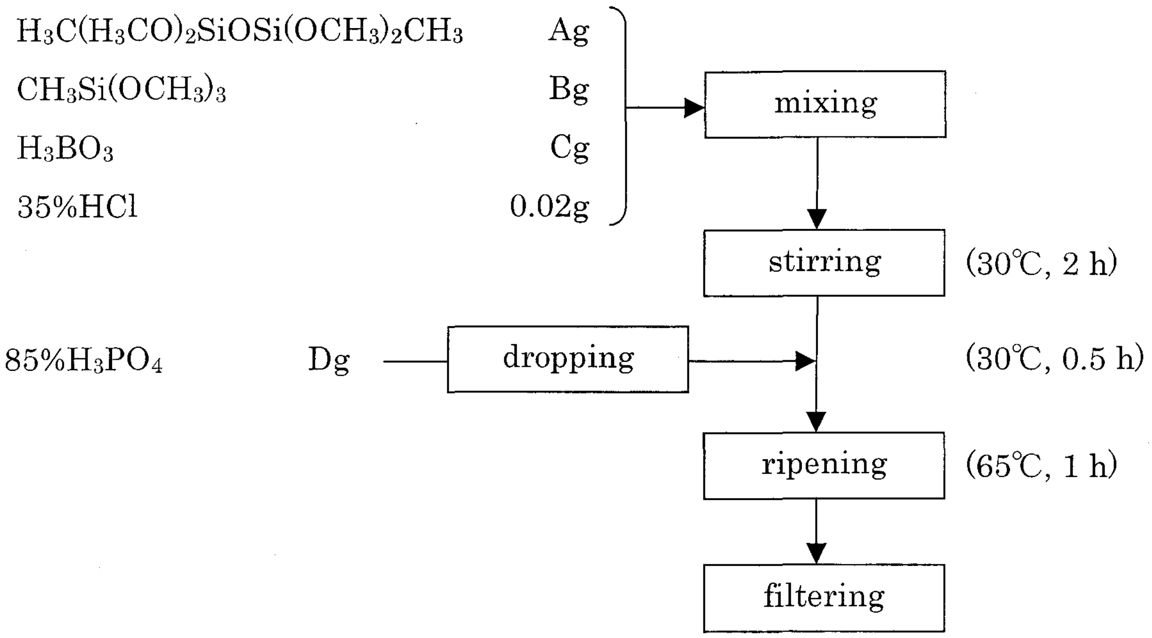


Fig. 4-1. Preparation procedure of the metal alkoxide oligomers.

Table 4-1. Gel compositions and amounts of reagents used in the preparation of metal alkoxide oligomers.

Solution	Gel compositions	Amounts of reagents (g)			
No.	(mol%)	A	B	C	D
1	$95SiO_2$-$5P_2O_5$	107.4	0	0	5.8
2	$90SiO_2$-$10P_2O_5$	0	122.5	0	11.5
3	$85SiO_2$-$15P_2O_5$	0	115.7	0	17.3
4	$80SiO_2$-$20P_2O_5$	0	108.9	0	23.1
5	$90SiO_2$-$10B_2O_3$	101.8	0	6.2	0
6	$85SiO_2$-$15B_2O_3$	96.1	0	9.3	0
7	$80SiO_2$-$20B_2O_3$	0	108.9	12.4	0
8	$90SiO_2$-$5P_2O_5$-$5B_2O_3$	101.8	0	3.1	5.8
9	$85SiO_2$-$7.5P_2O_5$-$7.5B_2O_3$	0	115.7	4.6	8.6
10	$80SiO_2$-$10P_2O_5$-$10B_2O_3$	0	108.9	6.2	11.5

A: $H_3C(H_3CO)_2SiOSi(OCH_3)_2CH_3$ B: $CH_3Si(OCH_3)_3$
C: H_3BO_3 D: 85% H_3PO_4 solution

Solutions with a molar ratio of n:1:0.01 in oligomer reagents, methanol, and acetic acid were prepared with n being 0.5, 0.1, 0.03, and 0.01. To this solution, 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) was added as a property-enhancer with a molar ratio of 0.005 to prepare the property-enhancer added oligomer composites. Into moisture-conditioned specimens, the prepared solution was impregnated at 20 ℃ under a reduced pressure (15 mmHg) for three days. The treated specimens were then placed in an oven controlled to be 65 ℃ for 24 h and 105 ℃ for another 24 h for aging of the gel.

4.2.3 Evaluation of wood-inorganic composites

The weight percent gain (WPG) and bulking coefficient (B) of the composites were determined by the same procedure described in Chapters 1 and 2, respectively.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made on the composites by the same procedure described in Chapter 1.

To evaluate the stability of the gel against weathering, the prepared composites were subject to a leaching test. One piece of the composites [30 (R) × 30 (T) × 5 (L) mm] was placed in 250 ml of distilled water (20-24 ℃) in 300 ml beaker and stirred at 160±3 r.p.m. for 1h and 4h. After the test, the specimens were vacuum-dried in the oven at 60 ℃, and the oven-dried weights were determined. The weight loss percentages of the WPG were then computed from an equation of (4-1).

$$\text{Weight loss percentages of the WPG}(\%)=(WPG-WPG')/WPG\times 100 \qquad (4\text{-}1)$$

where WPG and WPG' are, respectively, weight percent gains before and after the leaching test.

For studying the carbonized composite specimens, samples were burned with a match until they vanished. Subsequently, the carbonized portions of the specimens were cut with a razor knife to observe carbonized inner portion, and the exposed transverse surfaces were studied with a JOEL scanning electron microscope (JSM-T330A).

4.3 RESULTS AND DISCUSSION

4.3.1 Vaporization of the metal alkoxide oligomers

The preparation of the wood-inorganic composites by the sol-gel process of metal alkoxides is based on the specific reaction of their hydrolysis and polycondensation. Unreacted metal alkoxides are, therefore, expected to be vaporized to remove during the treatment. However, in the oligomer reaction system, unreacted oligomers can not be expected to be entirely removed due to their high boiling temperatures. Therefore, a vaporization of the metal alkoxide oligomers was first studied prior to the preparation of wood-inorganic composites.

Figure 4-2 shows the changes of various metal alkoxide oligomers for vaporization treatment at 105 ℃. Just for comparison, the results of TEOS, TMP, and TMB were also plotted in the figure. Although TEOS, TMP, and TMB were vaporized entirely by 4 h treatment, oligomers were only vaporized to a certain extent with some gel remaining. This implies that in the preparation of the wood-inorganic composites, the unreacted TEOS, TMP or TMB can be vaporized to be removed during the aging treatment so that the gel formed within the cell walls is due specifically to the sol-gel process. However, in the reaction system with metal alkoxide oligomers, the gel is formed not only by the sol-gel reaction but also by non-specific, unvaporized gel as seen in Fig. 4-2. Therefore, the inorganic substances would deposit specifically within the cell wall by sol-gel reaction but also deposit all over in the wood cells by non-specific unvaporized gel. Resultingly, inorganic gel in the oligomer reaction system is formed not only within the cell walls but also in the cell lumens.

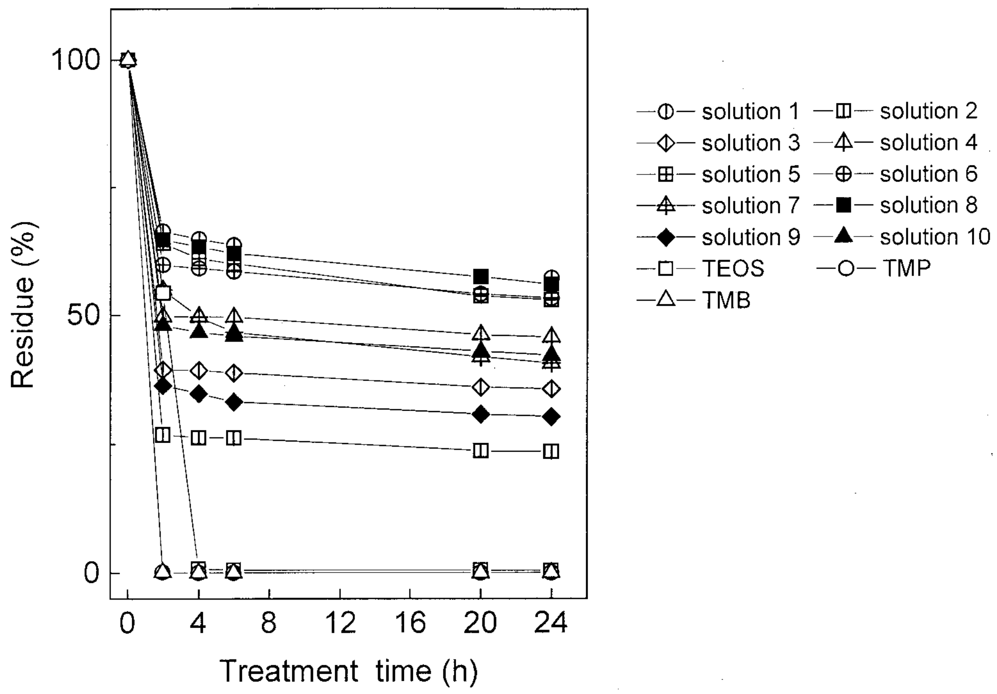


Fig. 4-2. Changes of various metal alkoxide oligomers for vaporization treatment at 105℃.

Figure 4-3 shows the relationship between the WPG of the composite and the molar ratio of the oligomer (No.1, $95SiO_2$-$5P_2O_5$, in Table 4-1) to methanol. The WPG of the composite was found to increase with increasing the molar ratio of oligomer to methanol. Therefore, the WPGs of obtained composites would depend on the oligomer concentration in the reaction medium. From this result, all the wood-inorganic composites from metal alkoxide oligomers shown in Table 4-1 were fixed to be prepared at the molar ratio of oligomer to methanol being 0.03 to 1. In this fixed condition, the WPG may be below 30% and still the fire-resisting property of wood can be expected to be enhanced without losing the porous structure characteristic of wood.

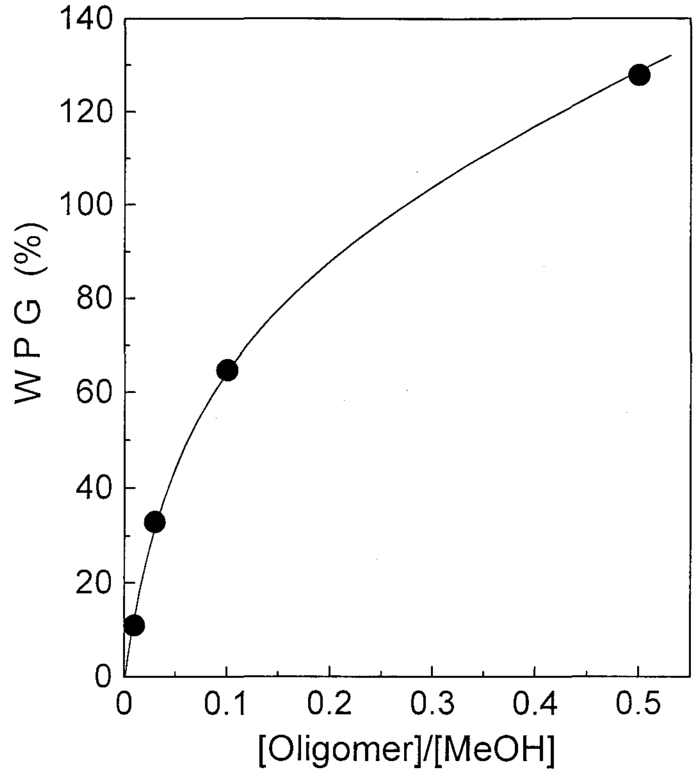


Fig. 4-3. Relationship between the WPG of the composite and the molar ratio of the metal alkoxide oigomer (No.1, $95SiO_2$-$5P_2O_5$, in Table 4-1) to methanol.

4.3.2 Wood-inorganic composites from oligomers

Table 4-2 shows the WPG and B of various composites prepared at the molar ratio of oligomer/methanol being 0.03/1. For these composites, SEM observations were made and the results were shown in Fig. 4-4. Just for comparison, the results of untreated wood (a) and the SiO_2-P_2O_5 composites from metal alkoxide monomers (b) were also shown in the figure. For the composites from oligomers (c), mol% ratios are shown as in $95SiO_2$-$5P_2O_5$ to distinguish from SiO_2-P_2O_5 composites from metal alkoxide monomers. In the

SiO_2-P_2O_5 composites from metal alkoxide monomers (b), the inorganic substances could not be observed in the cell lumens as seen in the untreated wood. However, in SiO_2-P_2O_5 composites from oligomers (c), the inorganic substances could be seen in the cell lumens. These results of SEM observations could ensure the assumption mentioned above. That is, inorganic gel in the oligomer reaction system is formed not only within the cell walls but also in the cell lumens.

4.3.3 Thermal properties of various wood-inorganic composites

As an easy method to understand the fire-resistance of the composites from oligomers, SEM observations were made on $95SiO_2$-$5P_2O_5$ composites

Table 4-2. WPG and B of various wood-inorganic composites.

Solution No.	Wood-inorganic composite (mol%)	WPG (%)	B (%)
1	$95SiO_2$-$5P_2O_5$	33.6	0.8
2	$90SiO_2$-$10P_2O_5$	27.9	1.2
3	$85SiO_2$-$15P_2O_5$	28.3	2.1
4	$80SiO_2$-$20P_2O_5$	27.6	2.0
5	$90SiO_2$-$10B_2O_3$	28.1	1.0
6	$85SiO_2$-$15B_2O_3$	28.1	0.8
7	$80SiO_2$-$20B_2O_3$	23.7	3.8
8	$90SiO_2$-$5P_2O_5$-$5B_2O_3$	30.6	1.3
9	$85SiO_2$-$7.5P_2O_5$-$7.5B_2O_3$	27.3	1.8
10	$80SiO_2$-$10P_2O_5$-$10B_2O_3$	25.9	1.9

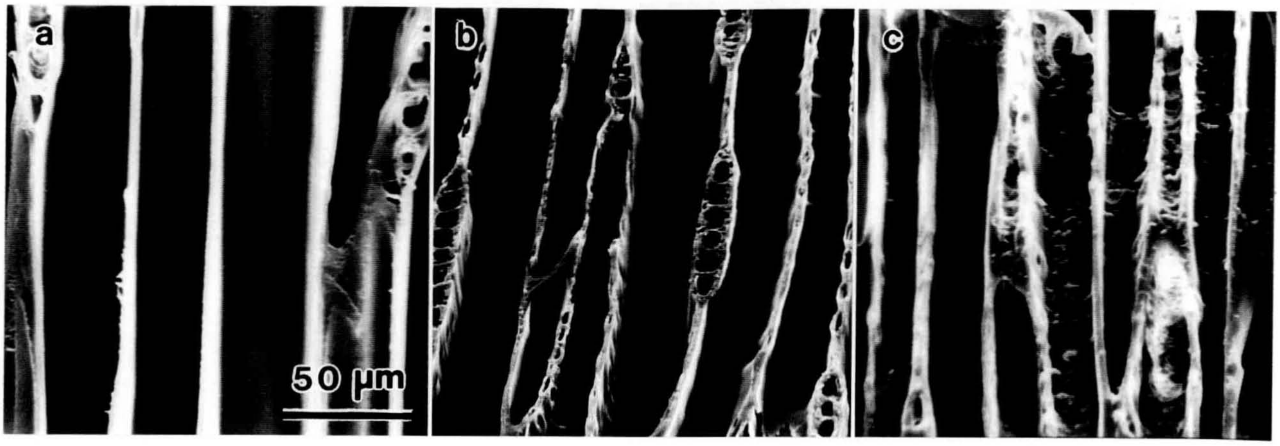


Fig. 4-4. Comparisons of SEM micrographs of untreated wood (a), SiO_2-P_2O_5 composites from monomers with 16.9 WPG (b) and $95SiO_2$-$5P_2O_5$ composites from oligomers with 32.9 WPG (c).

after burning, and the obtained micrographs are shown in Fig. 4-5. Although untreated wood specimens (a) are very thin in residual cell walls, $95SiO_2$-$5P_2O_5$ composites from oligomers (c) are very thick, as in SiO_2-P_2O_5 composites from monomers (b).

Furthermore, the results by thermogravimetric (TG) analyses and differential thermal analyses (DTA) show the evidence for the high fire-resistance of composites from oligomers. Figure 4-6 shows one example from the obtained TG curves of the various binary SiO_2-P_2O_5 composites from oligomers. For comparison, the result of the SiO_2-P_2O_5 composites from metal alkoxide monomers from Chapter 3 is also included. Compared with the untreated wood, the TG curves of various SiO_2-P_2O_5 composites from oligomers are shifted to the lower temperature for flaming and the greater residues are resulted after flaming. Although the WPGs of those composites from oligomers were slightly higher than those from monomers, the former composites show the enhanced fire-resisting effect as in the latter composite.

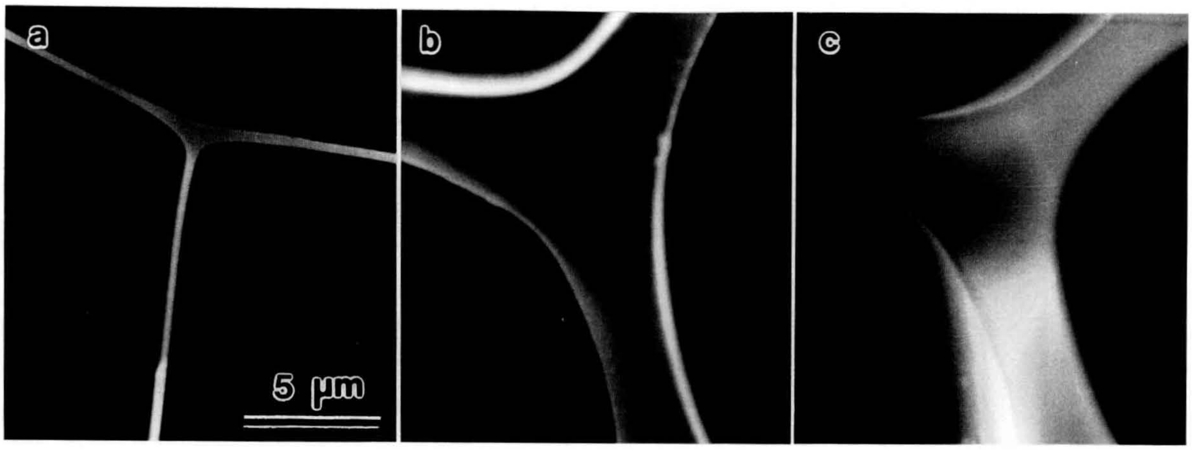


Fig. 4-5. Comparisons of carbonized wood-inorganic composites after burning. (a) Untreated wood, (b) SiO_2-P_2O_5 composites from monomers (16.9 WPG), (c) $95SiO_2$-$5P_2O_5$ composites from oligomers (32.9 WPG).

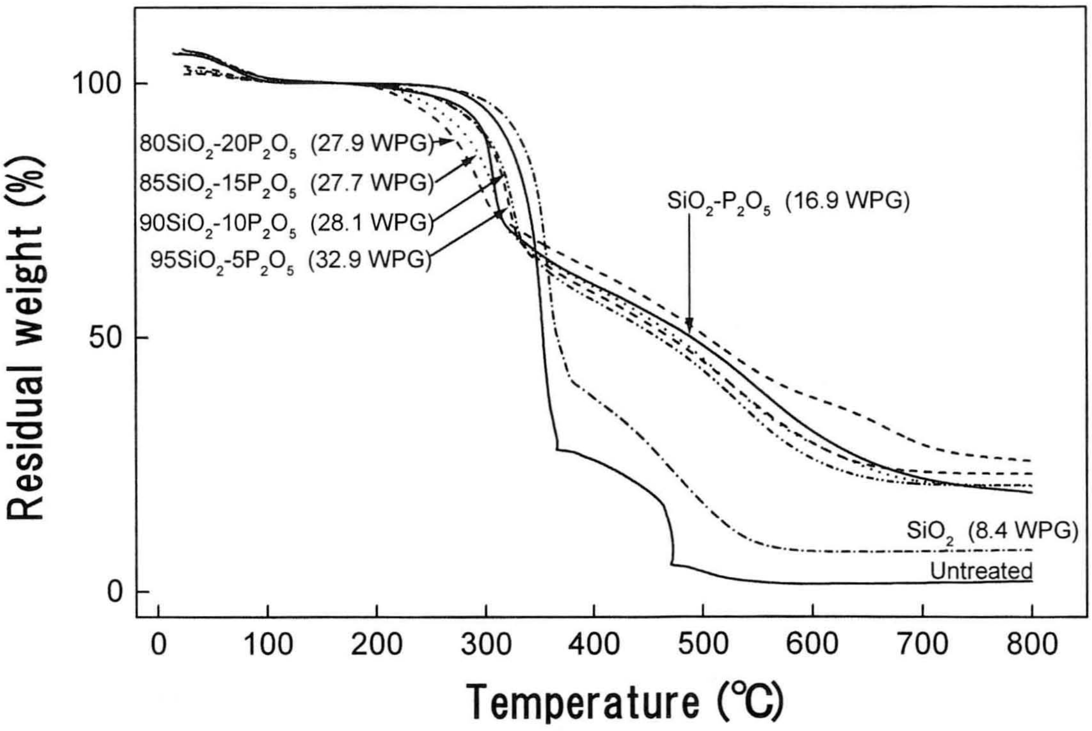


Fig. 4-6. TG curves for various SiO_2-P_2O_5 composites prepared from metal alkoxide oligomers.

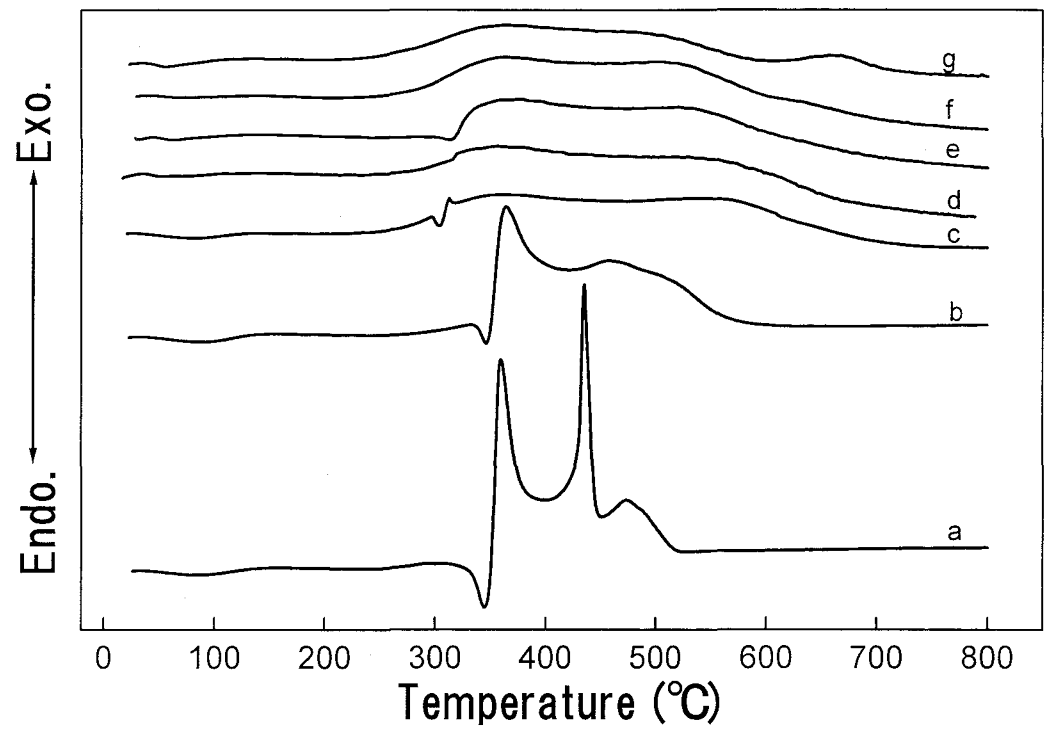


Fig. 4-7. DTA curves for various SiO_2-P_2O_5 composites.
(a) Untreated (b) SiO_2 (8.4 WPG) (c) SiO_2-P_2O_5 (16.9 WPG)
(d) $95SiO_2$-$5P_2O_5$ (32.9 WPG) (e) $90SiO_2$-$10P_2O_5$ (28.1 WPG)
(f) $85SiO_2$-$15P_2O_5$ (27.7 WPG) (g) $80SiO_2$-$20P_2O_5$ (27.9 WPG)

Figure 4-7 shows the DTA curves of various SiO_2-P_2O_5 composites from oligomers (d and e). The prominent exothermic peaks observed in the untreated wood for flaming and glowing can not be seen in these DTA curves. However, broad exothermic curves continued to about 600 ℃ as seen in SiO_2-P_2O_5 composites from metal alkoxides (c in Fig. 4-7). From these results, it was revealed that various SiO_2-P_2O_5 composites from oligomers have a great fire-resisting effect as observed in the SiO_2-P_2O_5 composites from metal alkoxides monomers. This fire-resisting effects is due to dehydration reaction with phosphorous compounds as discussed elsewhere (Browne 1958, Miyafuji and Saka 1996).

Figure 4-8 shows the TG curves of various binary SiO_2-B_2O_3 composites from oligomers. In this case, again the previous result of the SiO_2-B_2O_3

composites from metal alkoxide monomers from Chapter 3 is also included for comparison. The mol% ratios such as $90SiO_2$-$10B_2O_3$ are prepared from metal alkoxide oligomers. Compared with the untreated wood, the TG curves of these SiO_2-B_2O_3 composites from oligomers were shifted to the upper temperature for flaming. However, the residual weights of SiO_2-B_2O_3 composites from oligomers were lower after flaming than those composites from metal alkoxides monomers.

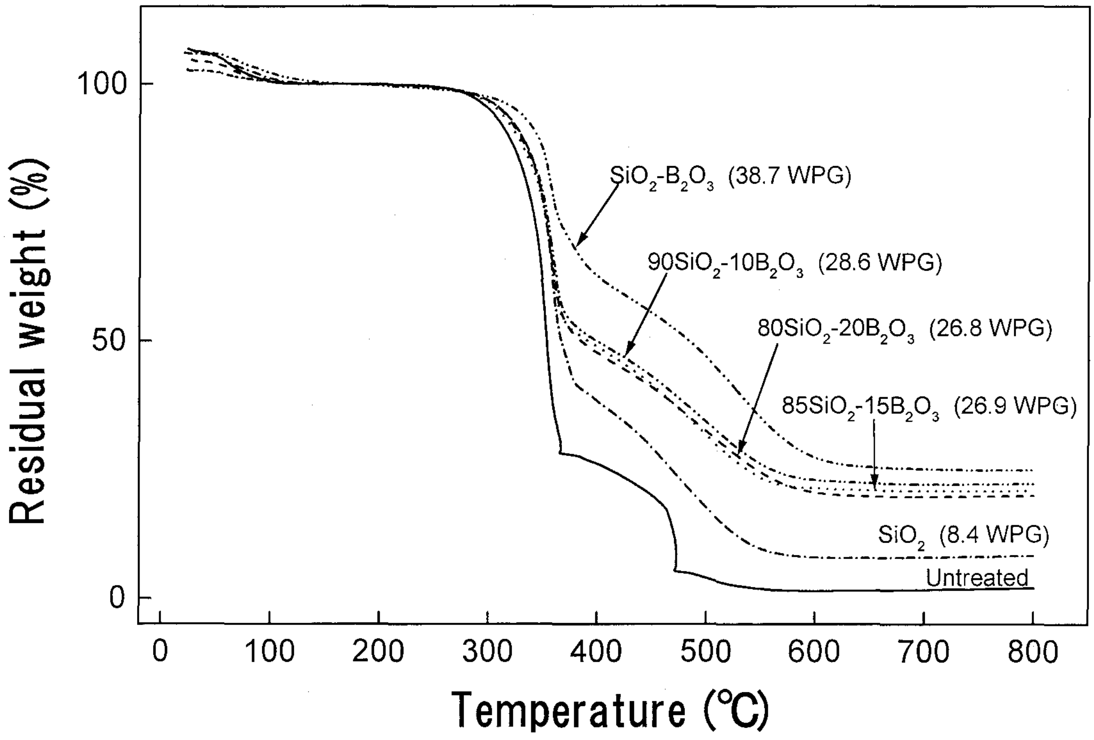


Fig. 4-8. TG curves for various SiO_2-B_2O_3 composites prepared from metal alkoxide oligomers.

Figure 4-9 shows the DTA curves of various SiO_2-B_2O_3 composites from oligomers (d and e). As in Fig. 4-7, the exothermic peak for flaming is weakened compared with untreated wood, and the peak for glowing disappears. But these peaks are slightly higher in oligomers (d and e), compared with SiO_2-B_2O_3 composites from metal alkoxide monomers (c in Fig.

4-9). These results of TG and DTA indicate that the SiO_2-B_2O_3 composites from oligomers are slightly inferior in fire-resistance to the SiO_2-B_2O_3 composites from metal alkoxide monomers. The fire-resisting effects in these gels are due perhaps to physical barriers formed by boric and silicic compounds that were melted and coated over the cell wall components (Browne 1958, Miyafuji and Saka 1996).

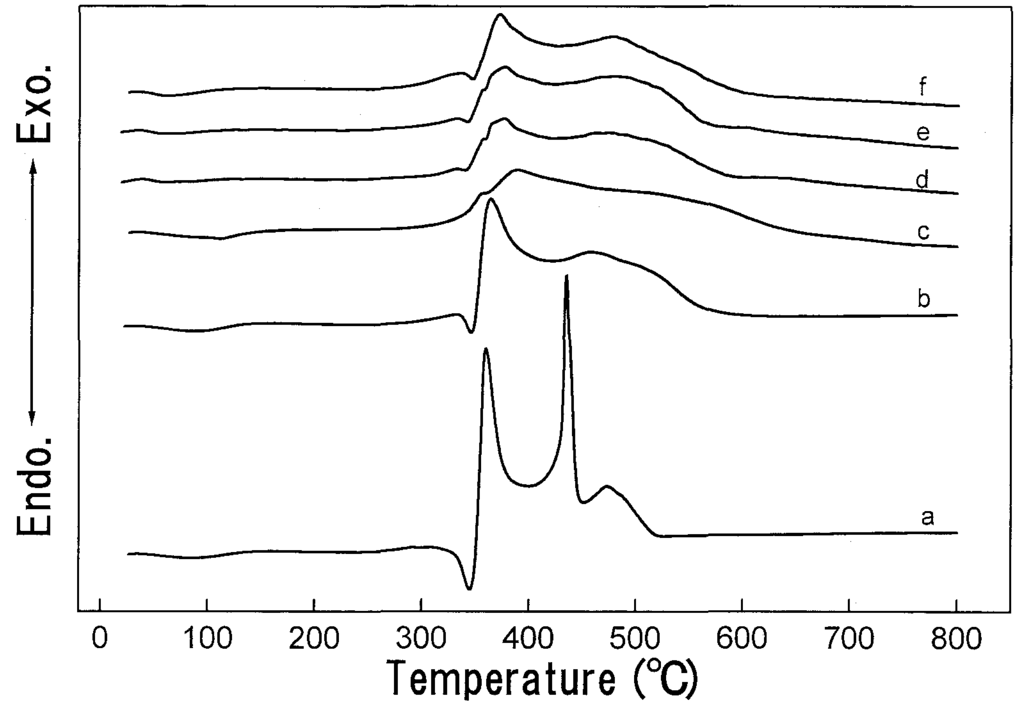


Fig. 4-9. DTA curves for various SiO_2-B_2O_3 composites.
(a) Untreated (b) SiO_2 (8.4 WPG) (c) SiO_2-B_2O_3 (38.7 WPG)
(d) $90SiO_2$-$10B_2O_3$ (28.6 WPG) (f) $85SiO_2$-$15B_2O_3$ (26.9 WPG)
(g) $80SiO_2$-$20B_2O_3$ (26.8 WPG)

Figure 4-10 shows the TG curves of the various ternary SiO_2-P_2O_5-B_2O_3 composites from oligomers. The TG curves clearly show that these ternary composites are all shifted to the lower temperature for flaming with the greater residues after flaming compared with untreated wood or SiO_2 composites. However, the closer inspection indicates that SiO_2-P_2O_5-B_2O_3

composites from oligomers are lower in its residual weight after flaming, compared with the composites from metal alkoxide monomer. However, considering the difference of the WPGs in these composites, the fire-resisting effect of these composites can be assumed to be essentially the same.

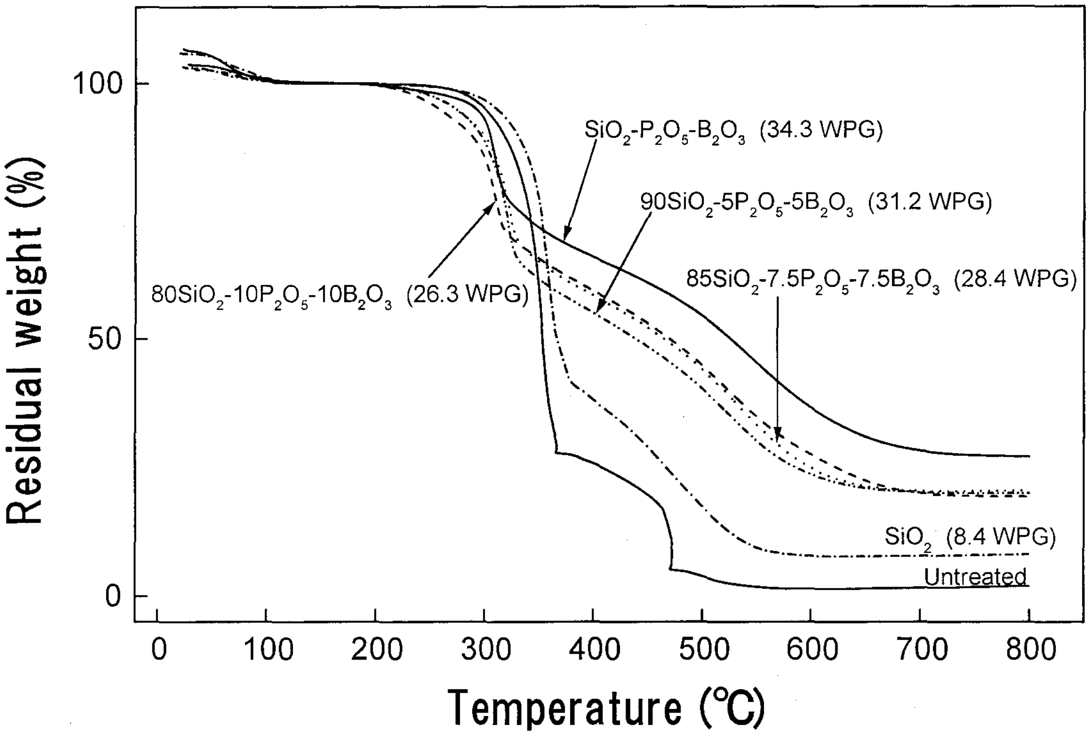


Fig. 4-10. TG curves for various SiO_2-P_2O_5-B_2O_3 composites prepared from metal alkoxide oligomers.

Figure 4-11 shows the DTA curves of various SiO_2-P_2O_5-B_2O_3 composites from oligomers (d and e). As seen in Figs. 4-7 and 4-9, the prominent exothermic peak for flaming and glowing can not be seen and broad exothermic curves continue to about 600 ℃. From these results, various SiO_2-P_2O_5-B_2O_3 composites from oligomers were also found to have the enhanced fire-resisting properties, due to chemical effects of phosphorous compounds as well as physical effect of boric and silicic compounds described above (Browne 1958, Miyafuji and Saka 1996).

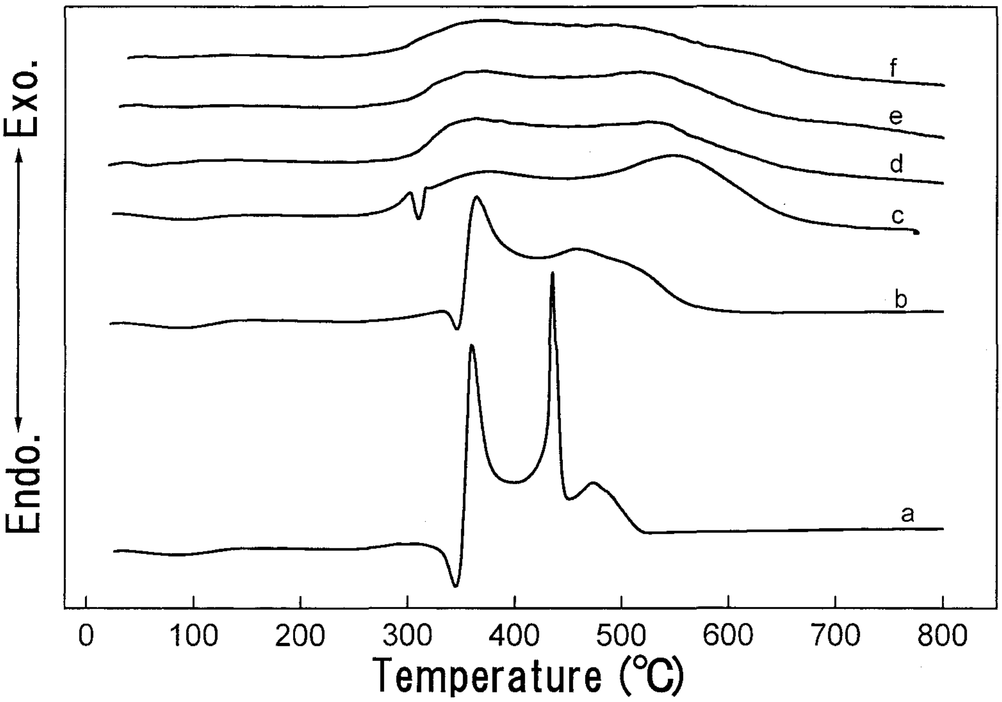


Fig. 4-11. DTA curves for various SiO_2-P_2O_5-B_2O_3 composites.
(a) Untreated (b) SiO_2 (8.4 WPG) (c) SiO_2-P_2O_5-B_2O_3 (34.3 WPG)
(d) $90SiO_2$-$5P_2O_5$-$5B_2O_3$ (31.2 WPG)
(f) $85SiO_2$-$7.5P_2O_5$-$7.5B_2O_3$ (28.4 WPG)
(g) $80SiO_2$-$10P_2O_5$-$10B_2O_3$ (26.3 WPG)

4.3.4 Stability of the gel in the composites against weathering

Figures 4-12, 4-13, and 4-14 show the results of the leaching test on various SiO_2-P_2O_5, SiO_2-B_2O_3, and SiO_2-P_2O_5-B_2O_3 composites from alkoxide oligomers. Just for comparison, the results of the composites from monomers are also plotted in the figures. From these results, various composites from oligomers were found to prevent the gel from leaching effectively. Particularly, as shown in Figs. 4-13 and 4-14, SiO_2-B_2O_3 and SiO_2-P_2O_5-B_2O_3 composites from oligomers can prevent the gel from leaching to a greater extent than the composites from monomers and even the HFOETMOS added-composites from monomers. This may be because the starting oligomer reagents are already composed of siloxane oligomers with phosphorous and/or boric hydroxide residues so that in a molecular level, these ternary or binary components are well mixed and covalently bonded. These oligomers are further hydrolyzed and polycondensed during the preparation of the wood-inorganic composites. Thus, the prepared gel in wood must be more stable than that from metal alkoxide monomers. This would be a reason why the composites prepared from oligomers are more stable against leaching.

The further stabilization of the gel was tried to be made by applying HFOETMOS to the oligomer reaction systems. It is clear in Fig. 4-14 that HFOETMOS added ternary composites from oligomers are most stable with the small loss percentage of the WPG.

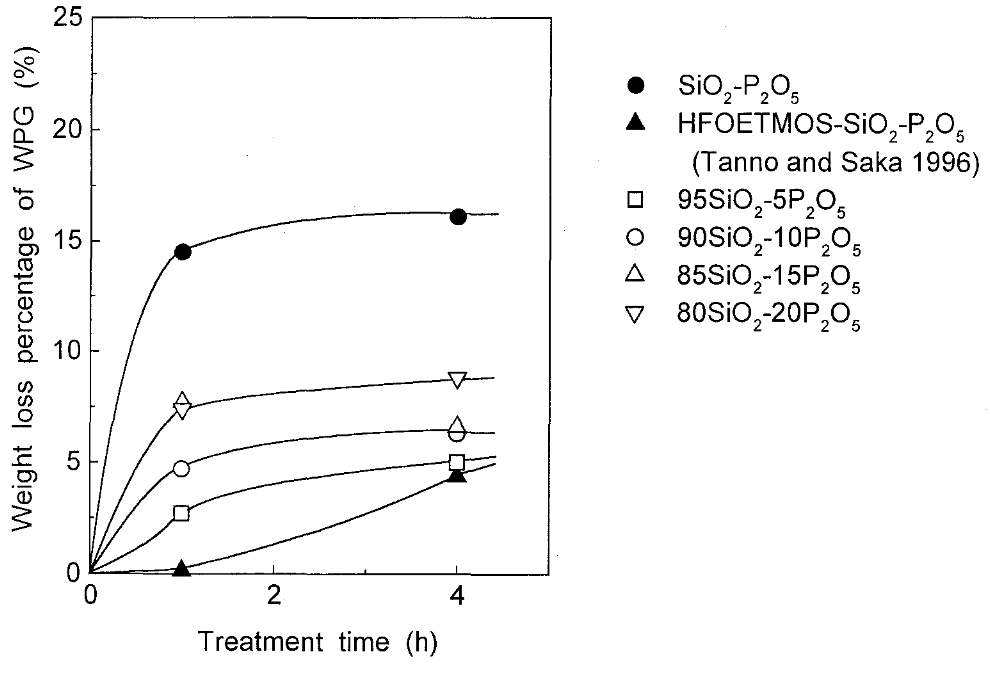


Fig. 4-12. Changes of the weight loss percentage of the WPG in the various SiO_2-P_2O_5 wood-inorganic composites.

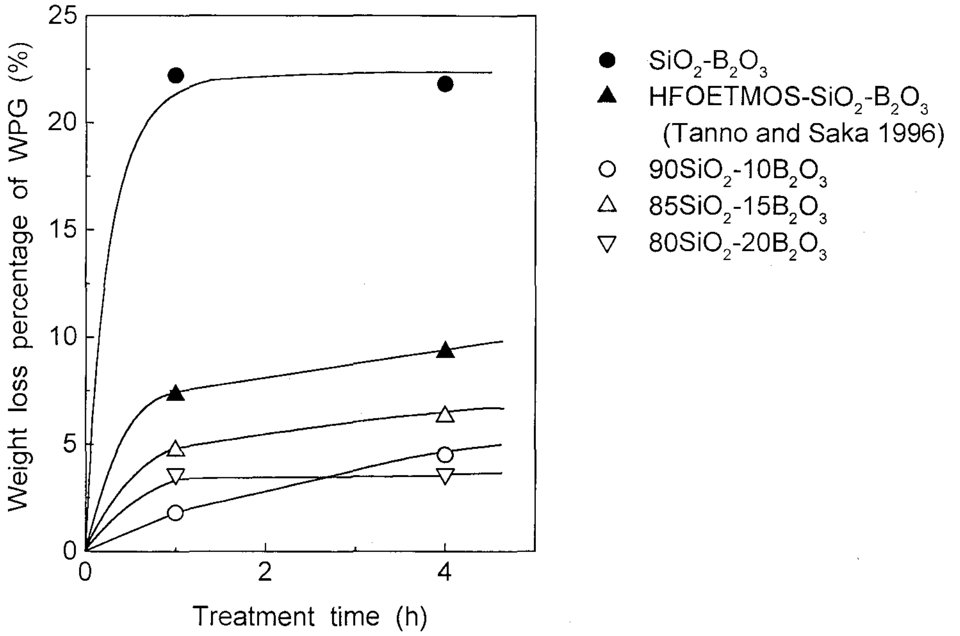


Fig. 4-13. Changes of the weight loss percentage of the WPG in the various SiO_2-B_2O_3 wood-inorganic composites.

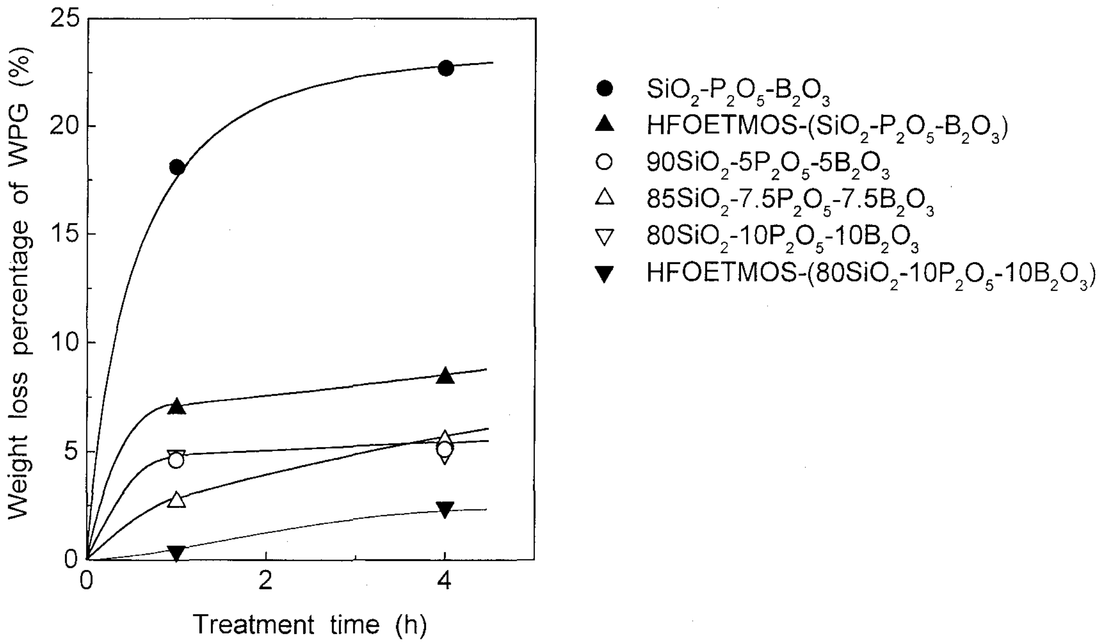


Fig. 4-14. Changes of the weight loss percentage of the WPG in the various SiO_2-P_2O_5-B_2O_3 wood-inorganic composites.

4.4 SUMMARY

In this chapter, some silicon alkoxide oligomers with phosphorous and/or boric hydroxide residues were prepared and applied for the SiO_2-P_2O_5-B_2O_3 wood-inorganic composites preparation. The obtained composites revealed a high fire-resistance and prevent the gel from leaching. Additionally, the prepared oligomers are non-toxic so that the environmental safety for preparation was achieved. By adding HFOETMOS to oligomer reaction system, the obtained composites could improve further the anti-leachability of the P_2O_5 and B_2O_3 gels.

Chapter 5

Topochemistry of SiO_2 Wood-Inorganic Composites For Enhancing Water-Repellency

5.1 INTRODUCTION

For adding water-repellent property to wood, the author has applied 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) to the reaction system for various wood-inorganic composites (Saka and Tannno 1996, Saka and Ueno 1997, Tanno *et al.* 1997, 1998). In Chapter 4, it was also consequently revealed that HFOETMOS-added SiO_2-P_2O_5-B_2O_3 wood-inorganic composites from metal alkoxide oligomers could attain the high water-repellent property. With this property enhanced, these composites could have prevented P_2O_5 or B_2O_3 gel from leaching out and maintained their high fire-resisting property after severe weathering test.

However, a mechanism of their property-enhancement for these wood-inorganic composites with HFOETMOS has not been confirmed yet. In this chapter, therefore, various HFOETMOS woods and HFOETMOS-SiO_2 wood-inorganic composites were prepared to elucidate the mechanism of water-repellent property enhancement. By evaluating their water-repellency and the fluorine distribution from HFOETMOS in these composites by scanning electron microscopy coupled with an energy-dispersive X-ray analysis (SEM-EDXA) (Saka 1992b), the topochemistry of the HFOETMOS-SiO_2 wood-inorganic composites were studied for enhancing water-repellency of wood.

5.2 MATERIALS AND METHODS

5.2.1. Wood specimens

The wood specimens were prepared by the same procedure described in Chapter 1.

5.2.2. Preparation of various HFOETMOS-SiO_2 wood-inorganic composites

Solutions were prepared with a molar ratio of 1:1:0.01 in tetraethoxysilane (TEOS) or methyltrimethoxysilane (MTMOS), ethanol or methanol and acetic acid for preparing two kinds of SiO_2 wood-inorganic composites from TEOS or MTMOS. To these solutions, property-enhancer, 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS), was added with a molar ratio of 0.05, 0.01, 0.004 and 0.001 to TEOS or MTMOS to prepare HFOETMOS-SiO_2 wood-inorganic composites from TEOS or MTMOS. TEOS, MTMOS and HFOETMOS were provided from Shin-Etsu Chemical Co., Ltd.

Furthermore, solutions were prepared with a molar ratio of 0.03, 0.01, 0.006 or 0.001 of MTMOS in the 1 : 0.01 : 0.004 molar ratio of methanol, acetic acid and HFOETMOS to prepare the HFOETMOS-SiO_2 wood-inorganic composites with various weight percent gains (WPGs). To achieve the same weight concentration of HFOETMOS in these reaction mediums, MTMOS was displaced at an equal weight with methanol, as its molar ratio was decreased. Just for comparison, HFOETMOS-treated woods were also prepared with several solutions of HFOETMOS in methanol and acetic acid with 0.03, 0.01, 0.004, 0.001 or 0.0005 of HFOETMOS in the 1 : 0.01 molar ratio of methanol and acetic acid.

Subsequently, into moisture-conditioned specimens, the prepared solutions above were impregnated at 20 ℃ under a reduced pressure (15 mmHg) for three days. The impregnated specimens were then placed in an oven controlled to be 60 ℃ for 24 h and 105 ℃ for another 24 h for aging of the gel. For each treatment, four specimens were prepared.

5.2.3. Evaluation of wood-inorganic composites

The weight percent gain (WPG) and bulking coefficient (B) of the composites were determined by the same procedure described in Chapters 1 and 2, respectively.

The fluorine content in the obtained composites was determined by using fluorine ion selective electrode after decomposing the composites by oxygen flask combustion method (Hozumi and Akimoto 1971). From the determined fluorine content in the composites, the amount of fluorine added-on ($F_{added\text{-}on}$) was calculated, on an oven-dried weight basis, which can show the amount of fluorine added on to the non-treated wood basis.

To evaluate the water-repellent property of the composites, the specimens were placed in distilled water with weights under a normal pressure at 20℃, and changes in the weights of the prepared composites (W_1) due to water absorption were measured every other day. After 14 days, the untreated specimens were soaked further with distilled water under a reduced pressure for three days. The water content in such a water-saturated wood specimen (W_2) was considered to be maximal. The water absorption ratio (WAR) was then computed by the following equation (5-1) :

$$WAR = W_1/W_2 \qquad (5\text{-}1)$$

The contact angle (°) of the droplet over the prepared composites was measured from a photograph taken one minute after $2\mu l$ of water dropped over the cross section of the specimens.

For an energy-dispersive X-ray analysis, oven-dried specimens [0.7(R)×0.7(T)×3(L) mm] were soaked overnight in Spurr low viscosity epoxy resin consisting of a mixture of vinylcyclohexene dioxide, diglycidyl ether of polypropyleneglycol, nonenyl succinic anhydride, and dimethylaminoethanol (10:6:26:0.4 in weight ratio) and then cured in the usual way. The embedded specimens were subsequently sectioned with a glass knife, and the obtained transverse sections of $0.5\mu m$ in thickness were placed on a carbon-coated formvar film covered over single hole carbon grid. The sections were then studied with a scanning electron microscope (JEOL JSM-5800) coupled with an energy dispersive X-ray spectrometer (EDAX PHOENIX) (SEM-EDXA), based on the method described by Saka (1992b). The accelerating voltage was set at 15 kV. Additional variable conditions such as the distance of the X-ray detector from the specimens, the tilting angle of the specimens holder (0°), take-off angle, and working distance were all held constant throughout the entire study.

5.3 RESULTS AND DISCUSSION

5.3.1. HFOETMOS-SiO_2 wood-inorganic composites from TEOS or MTMOS

Table 5-1 shows the WPG and B for various HFOETMOS-SiO_2 wood-inorganic composites prepared from TEOS. The WPGs of these composites were found to increase slightly with increasing in the molar ratios of HFOETMOS to TEOS in a reaction medium. However, the B was found to be almost constant. Presumably, the increase in the WPG would be due to an increase in the HFOETMOS incorporated. For these composites, water absorption ratio (WAR) was measured as shown in Fig. 5-1. Although untreated wood specimens and SiO_2 composites from TEOS were saturated with water

Table 5-1. WPG and B for various HFOETMOS-SiO_2 wood-inorganic composites from TEOS.

	Molar ratio			
Composites	HFOETMOS	TEOS	WPG (%)	B(%)
SiO_2	0	1	7.6	4.0
HFOETMOS-SiO_2	0.001	1	7.9	4.3
	0.004	1	8.0	4.3
	0.01	1	8.1	4.2
	0.05	1	10.1	4.0

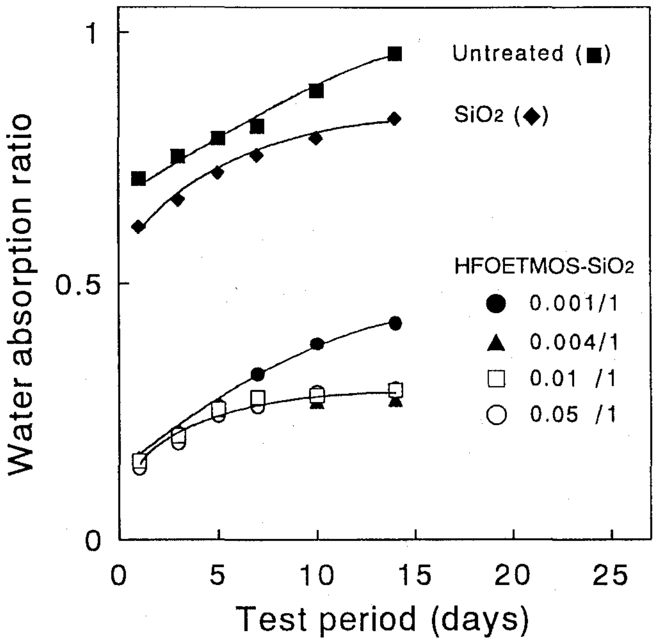


Fig. 5-1. Changes of water absorption ratios for various HFOETMOS-SiO_2 composites from TEOS with different molar ratio of HFOETMOS to TEOS.

after soaking for several days, HFOETMOS-SiO_2 composites absorbed water to a much lesser extent. Therefore, HFOETMOS-SiO_2 composites prepared from TEOS could attain high water-repellent property, especially for these with the molar ratios of HFOETMOS to TEOS being 0.004, 0.01 and 0.05.

Table 5-2 shows the WPG and B for various HFOETMOS-SiO_2 wood-inorganic composites prepared from MTMOS. Compared with the results in Table 5-1, the WPGs of these composites from MTMOS were found to be higher and constant to be above 25%. The B was also higher than that of the composites from TEOS (Table 5-1). This is because MTMOS has the higher hydrolysis and subsequent polycondensation rate than TEOS during sol-gel reaction, having resulted in the higher deposition of the SiO_2 gel. However, as shown in Fig. 5-2, the composites from MTMOS absorbed water as much as untreated wood specimens and the high water-repellent property

Table 5-2. WPG and B for various HFOETMOS-SiO_2 wood-inorganic composites from MTMOS.

	Molar ratio			
Composites	HFOETMOS	MTMOS	WPG (%)	B(%)
SiO_2	0	1	29.8	11.6
HFOETMOS-SiO_2	0.001	1	27.5	10.8
	0.004	1	27.8	10.9
	0.01	1	27.8	10.9
	0.05	1	25.9	10.8

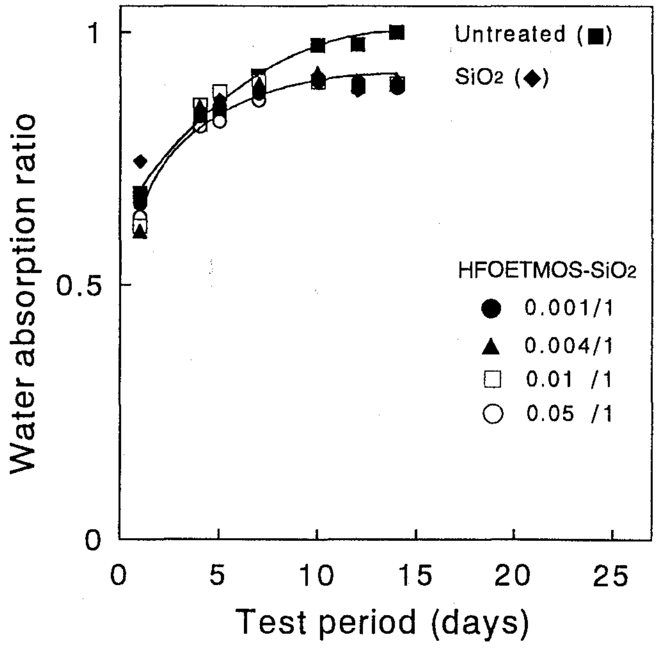


Fig. 5-2. Changes of water absorption ratios for various HFOETMOS-SiO_2 composites from MTMOS with different molar ratio of HFOETMOS to MTMOS.

could not be attained. This fact is different from the composites from TEOS in Fig. 5-1. To elucidate such a difference in the water-repellency between HFOETMOS-SiO_2 wood-inorganic composites prepared from TEOS and MTMOS, HFOETMOS woods and HFOETMOS-SiO_2 wood-inorganic composites from MTMOS with various WPGs were prepared and studied on their water-repellency.

5.3.2. HFOETMOS woods and their water-repellency

Table 5-3 shows the WPG, B and $F_{added\text{-}on}$ of the prepared HFOETMOS woods in which the WPG and $F_{added\text{-}on}$ were found to increase with the increase in the molar ratios of HFOETMOS to methanol in a reaction medium. However, the B was found to be constant to be nearly 0%. Since only substances present in the cell walls can contribute to the bulking of the specimens, HFOETMOS molecules would not be impregnated into the cell walls. To ensure this concept, the distribution of HFOETMOS-derived residues in the HFOETMOS woods was studied by SEM-EDXA analysis.

Table 5-3. WPG, B, $F_{added\text{-}on}$ and contact angle of water for various HFOETMOS woods.

	Molar ratio					Contact
Composites	HFOETMOS	MeOH	WPG (%)	B(%)	$F_{added\text{-}on}$ (%)	angle (°)
HFOETMOS	0.0005	1	2.0	0.1	0.8	140
	0.001	1	2.6	0.0	1.5	142
	0.004	1	8.4	0.0	4.8	143
	0.01	1	22.8	0.0	12.8	142
	0.03	1	32.3	0.1	16.4	142

Figure 5-3 shows the obtained SEM micrograph of the 0.5 μm thin section of HFOETMOS wood over which the distributions of fluorine and silicon were studied by SEM-EDXA along the line across the double cell walls. It is apparent that, although Si-Kα X-rays emission is detected with little concentration across the double cell walls, F-Kα X-rays are not uniform but concentrated at a boundary between the cell wall and cell lumen. This high concentration of F-Kα X-rays at the boundary must be due to the deposition of HFOETMOS-derived residues. Perhaps long hydrophobic fluorinated alkyl chain of HFOETMOS would have prevented its molecules from being impregnated into rather hydrophilic cell walls, and during the sol-gel reaction, the hydrolyzed HFOETMOS must be dehydrated to bind covalently each other at the surface of the cell lumens, with long fluorinated hydrophobic

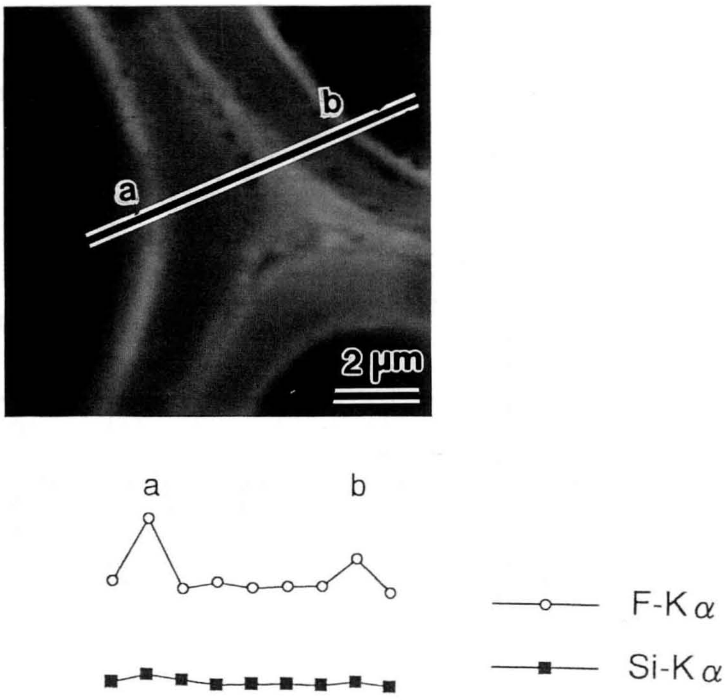


Fig. 5-3. SEM micrograph of the 0.5 μm thin section of HFOETMOS wood (upper) and obtained distributions of Si-Kα and F-Kα X-rays emitted along the line across the double cell walls (lower).

alkyl chains exposed. This would have enhanced water-repellent property of HFOETMOS woods.

For these HFOETMOS woods, the contact angle of water droplet and WAR of the specimens were measured to evaluate their water-repellency. The obtained contact angles on the prepared HFOETMOS woods are shown in Table 5-3. The contact angle on the untreated specimens could not be measured because the water drops were penetrated into the specimens as soon as they were dropped. However, all of the HFOETMOS woods showed the high contact angles above 140° .

Figure 5-4 shows a relationship between the molar ratio of HFOETMOS to methanol and the WAR of the HFOETMOS woods after five days soaking. HFOETMOS woods resulted in much less WAR, compared with untreated specimens (HFOETMOS/MeOH=0), indicating that HFOETMOS woods could have attained the enhanced water-repellent property. Furthermore, although the WAR decreased up to the molar ratio of about 0.004, it became constant afterward. This indicates that the optimum of its molar ratio must exist near 0.004 for the property enhancement of water-repellency.

5.3.3. HFOETMOS-SiO_2 wood-inorganic composites with various WPGs and their water-repellency

Table 5-4 shows the WPG, B and $F_{added\text{-}on}$ for the various HFOETMOS-SiO_2 wood-inorganic composites. The WPG of the obtained composites was found to increase with increasing in the molar ratio of MTMOS to methanol. The value of B was also found to increase with increasing in the molar ratio of MTMOS to methanol. However, these composites show almost the same $F_{added\text{-}on}$, because the molar ratio of HFOETMOS to methanol was 0.004 for all composites prepared. Therefore, SiO_2 gel formed within the cell walls would increase with increasing in the molar ratio of MTMOS to methanol.

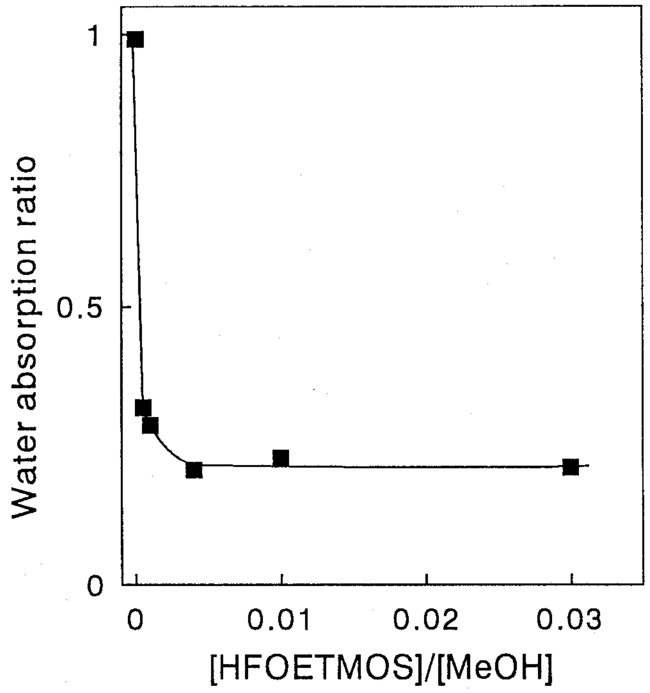


Fig. 5-4. A relationship between molar ratio of HFOETMOS to methanol and water absorption ratios of the HFOETMOS wood after five days soaking.

Table 5-4. WPG, B, $F_{added\text{-}on}$ and contact angle of water for various HFOETMOS-SiO_2 wood-inorganic composites.

	Molar ratio					Contact
Composites	MTMOS	MeOH*	WPG (%)	B(%)	$F_{added\text{-}on}$ (%)	angle (°)
HFOETMOS-SiO_2	0.001	1	10.5	1.6	5.4	146
	0.006	1	11.2	2.3	5.0	145
	0.01	1	11.6	2.8	4.9	146
	0.03	1	17.6	4.4	4.6	144

* The molar ratio of HFOETMOS to MeOH is 0.004 for all composites prepared.

For these composites, the contact angles measured (Table 5-4) were all to be above 140° , as in HFOETMOS woods. However, the changes of WAR in Fig. 5-5 are quite different among various HFOETMOS-SiO_2 composites. This result suggests that the degree of achieved water-repellency is different among these composites. Although not clear after one day soaking, it was obvious after three days soaking that the HFOETMOS-SiO_2 composites with molar ratio of 0.001:1 in MTMOS to methanol have the lowest WAR and thus highest water-repellent property compared with other composites.

To study this difference in water absorption ratios among various HFOETMOS-SiO_2 composites, the relationship between WAR after five days soaking and WPG was studied as in Fig. 5-6 for HFOETMOS-SiO_2 wood-inorganic composites. Consequently, the WAR was found to increase with increasing in the WPG of the HFOETMOS-SiO_2 composites. Although

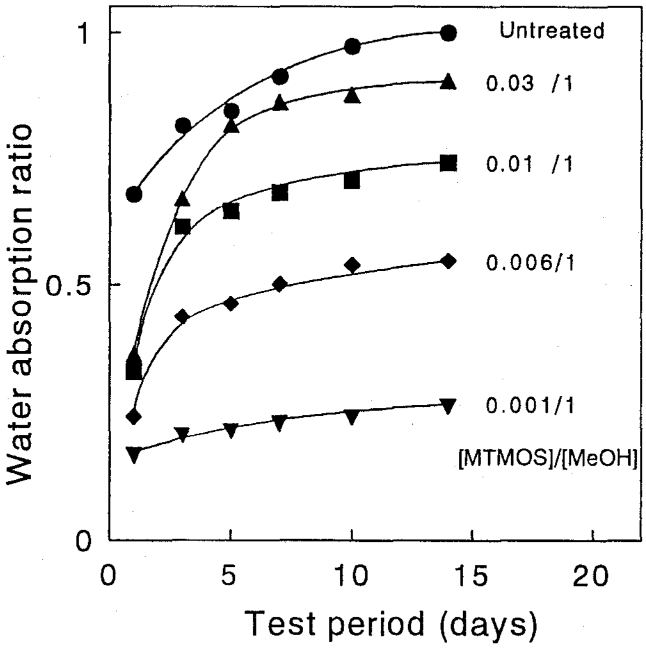


Fig. 5-5. Changes of water absorption ratios for various HFOETMOS-SiO_2 wood-inorganic composites with different molar ratio of MTMOS to methanol.

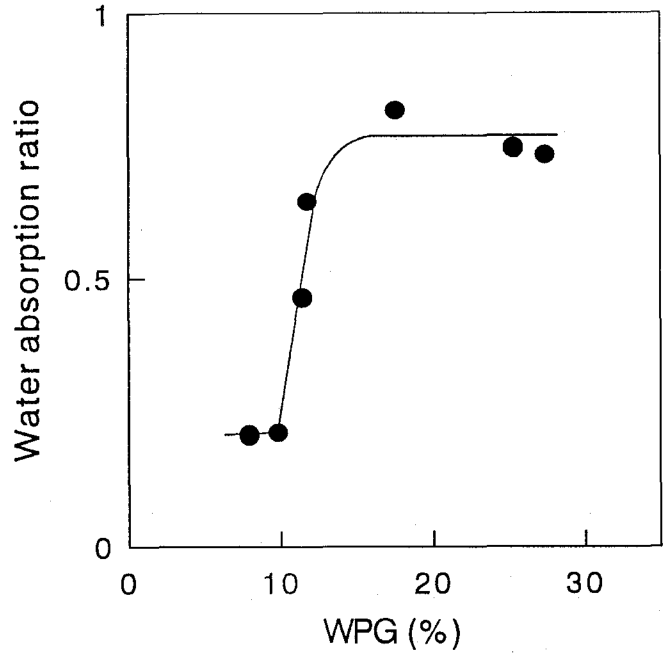
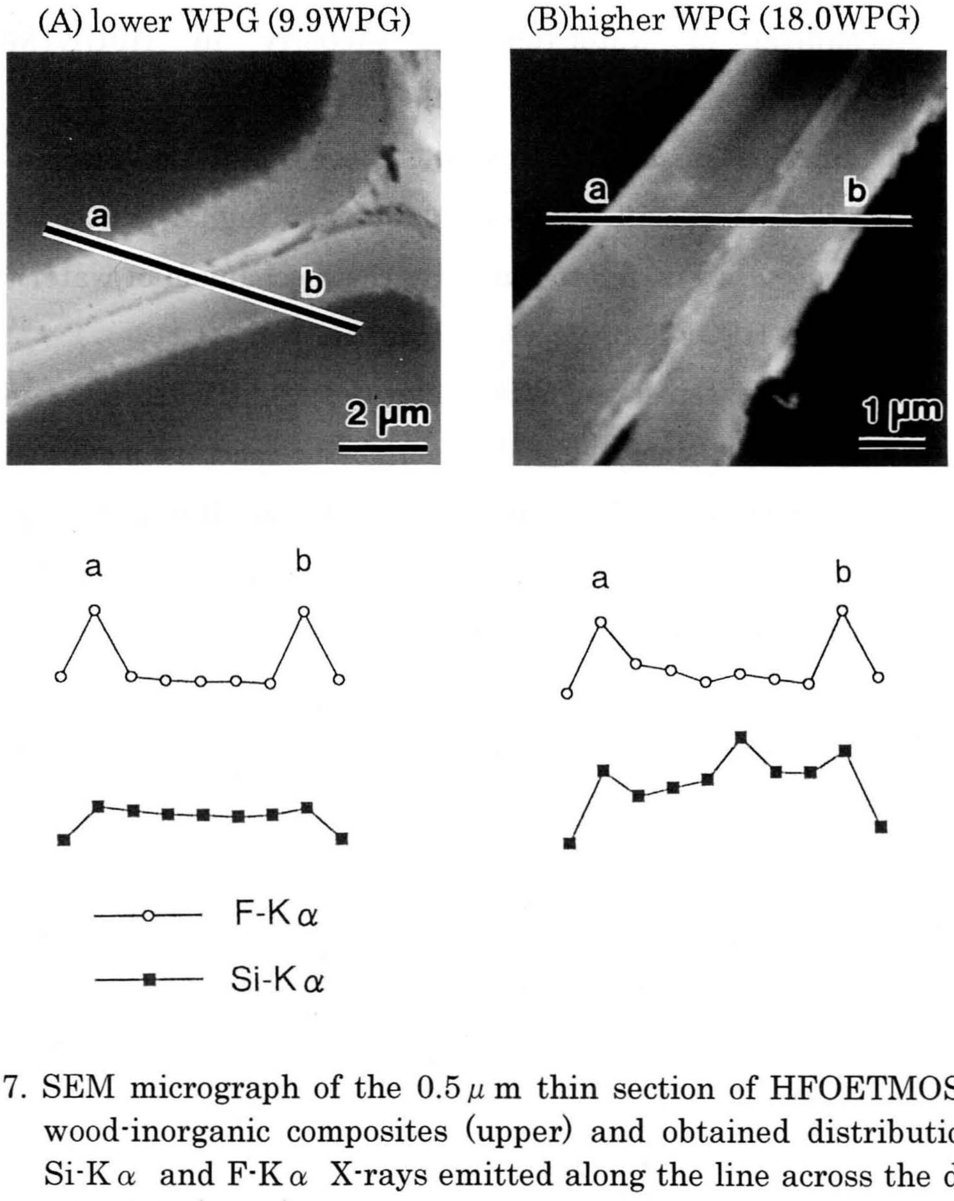


Fig. 5-6. A relationship between WPG and water absorption ratio for various HFOETMOS-SiO_2 wood-inorganic composites after their five days soaking.

$F_{added\text{-}on}$ in the obtained HFOETMOS-SiO_2 composites is almost the same as that in Table 5-4, the composites with the higher WPGs show the lower water-repellent property.

For the HFOETMOS-SiO_2 wood-inorganic composites with the higher and lower WPGs, therefore, SEM-EDXA analysis was made to study the distribution of SiO_2 gel and HFOETMOS-derived residues in the HFOETMOS-SiO_2 wood-inorganic composites. Figure 5-7 shows the SEM micrographs of HFOETMOS-SiO_2 wood-inorganic composites with the higher and lower WPGs and the obtained distributions of Si-Kα and F-Kα X-rays emitted along the line across the double cell walls. It is apparent that fluorine is concentrated at the boundary between the cell wall and cell lumen in both composites, as in HFOETMOS woods (Fig. 5-3). On the other hand, silicon in the composites with the lower WPG is almost uniformly distributed within the cell walls with certain concentrations. Silicon in the composites with the higher WPG was found to be distributed in a similar manner but slightly higher in its concentration at the intercellular layers and the boundary between the cell walls and cell lumens. These distributions of silicon in both composites would correspond to the distribution of SiO_2 gel from MTMOS because the Si-Kα from HFOETMOS-derived residue were detected with little concentration as shown in Fig. 5-3.


(A) lower WPG (9.9WPG)

(B)higher WPG (18.0WPG)

Fig. 5-7. SEM micrograph of the $0.5\,\mu$m thin section of HFOETMOS-SiO_2 wood-inorganic composites (upper) and obtained distributions of Si-Kα and F-Kα X-rays emitted along the line across the double cell walls (lower).

From these results, HFOETMOS-derived residues must be distributed at the boundary between the cell wall and the cell lumen, whereas MTMOS would be mostly impregnated into the cell walls and deposited within the cell walls as SiO_2 gel through the sol-gel reaction. This speculation can be well supported by the fact that the value of B of HFOETMOS-SiO_2 composites decreases with the decrease in the molar ratio of MTMOS to methanol, as shown in Table 5-4.

5.3.4. Mechanism of water-repellent property in HFOETMOS-SiO_2 wood-inorganic composites

Based on the results mentioned above, possible models of the HFOETMOS-SiO_2 composites with the lower and higher WPGs were schematically proposed in Fig. 5-8 to elucidate the mechanism of water-repellent property added to HFOETMOS-SiO_2 composites.

For the case of the lower WPG (Fig. 5-8(A)), HFOETMOS molecules would be impregnated into the cell lumens with reaction medium, but not into the cell walls due to its hydrophobic nature. During drying process, HFOETMOS molecules with high molecular weight (M.W.=568) would be deposited on the surface of the cell wall without being vaporized, whereas MTMOS molecules with low molecular weight (M.W.=136) could be readily vaporized. The surface of the cell walls would, thus, be covered with the long hydrophobic alkyl residue of the HFOETMOS, covalently bound with each other or with SiO_2 gel in the cell walls. Therefore, HFOETMOS-SiO_2 composites with the lower WPGs could attain the high water-repellent property.

For the case of the higher WPG (Fig. 5-8(B)), HFOETMOS molecules would be deposited on the surface of the cell wall in a similar manner. However, some of the SiO_2 sol tend to be formed in a reaction medium present in the cell lumens owing to the higher concentration of MTMOS. Such a sol with high molecular weight as in HFOETMOS molecules could not be vaporized

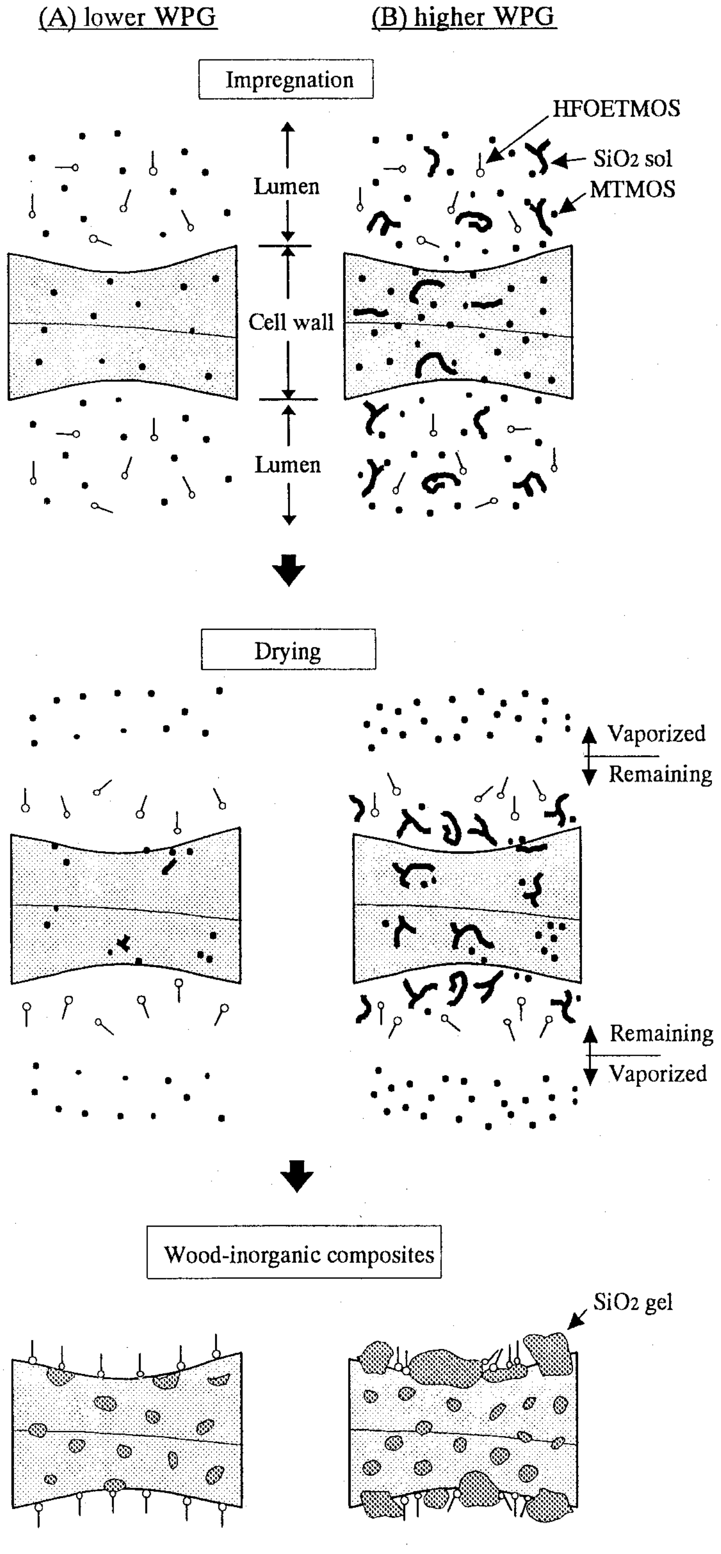


Fig. 5-8. Schematic illustration of HFOETMOS-SiO_2 wood-inorganic composites with the lower and higher WPGs. (The size of HFOETMOS, MTMOS, SiO_2 sol , SiO_2 gel and cell wall do not necessarily demonstrate the real scale in the composites.)

and would be deposited over the surface of the cell walls during drying process. Therefore, some of SiO_2 gel derived from such a sol would be distributed at the boundary between cell walls and cell lumens. A slightly higher concentration of silicon at the boundary in Fig. 5-7(B) can support this concept, and the gel would prevent HFOETMOS-derived residues from being exposed uniformly over the surface of wood cells as proposed in Fig. 5-8(B). Therefore, the composites with the higher WPG could not have attained the high water-repellent property as in the composites with the lower WPG.

5.4 SUMMARY

To elucidate the mechanism for enhancing the water-repellent property, the HFOETMOS-SiO_2 wood-inorganic composites with various WPGs were prepared, and the prepared composites with the lower WPG revealed the better property in water-repellency, whereas those with the higher WPG could not attain the high water-repellent property. SEM-EDXA analysis on these composites revealed that the HFOETMOS-derived residues were concentrated on the boundary between the cell wall and cell lumen in both composites with the lower and higher WPGs, while SiO_2 gel was almost uniformly distributed within the cell walls in the composites with lower WPG. SiO_2 gel in the composites with higher WPG was distributed in a similar manner but slightly higher in its concentration at the boundary between the cell wall and cell lumen. From these results, it was assumed that for the composites with lower WPG, the cell wall would be covered with the long hydrophobic alkyl residue of the HFOETMOS, whereas for the composites with higher WPG, SiO_2 gel formed in the cell lumen would have prevented HFOETMOS-derived residues from being exposed uniformly over the surface of cell wall. This may be why the different water-repellent properties were shown between the composites with higher and lower WPGs.

Consequently, for achieving the high water-repellency, it is important that HFOETMOS molecules distribute uniformly over the surface of cell walls and that the long hydrophobic alkyl chain of the HFOETMOS molecules cover the surface of cell walls. This suggests that the topochemical effect of HFOETMOS molecules exists for enhancement of properties in wood-inorganic composites.

Chapter 6

Na_2O-SiO_2 Wood-Inorganic Composites from Metal Alkoxide Monomers

6.1 INTRODUCTION

For enhancing the fire-resisting property of wood, trimethylphosphite (TMP) and/or trimethylborate (TMB) have been applied to the reaction system of the SiO_2 wood-inorganic composites, as described in previous chapters. On the obtained composites, the thermal properties were evaluated and these composites were found to have more enhanced fire-resisting properties than the SiO_2 composites.

In this chapter, therefore, as another trial to enhance the fire-resisting properties, the author has applied sodiummethoxide (SM) or sodiumacetate (SA) to a reaction system for the SiO_2 wood-inorganic composites. The prepared Na_2O-SiO_2 wood-inorganic composites were then studied on their fire-resisting properties by thermal analysis, and the effects of the sodium compound were evaluated on the fire-resistance of wood.

6.2 MATERIALS AND METHODS

6.2.1. Wood specimens

The wood specimens were prepared by the same procedure described in Chapter 1.

6.2.2. Preparation of the Na_2O-SiO_2 wood-inorganic composites

A solution was prepared with a molar ratio of 0.03:1:0.01 in methyltrimethoxysilane (MTMOS), methanol and acetic acid for preparing the SiO_2 wood-inorganic composites. To this solution, sodiummethoxide (SM) or sodiumacetate (SA) was added with molar ratios of 0.015, 0.030 and 0.060 to methanol to prepare the Na_2O-SiO_2 wood-inorganic composites with SM or

SA.

Subsequently, the prepared solutions above were impregnated into moisture-conditioned specimens at 20℃ under a reduced pressure (15mmHg) for three days. The impregnated specimens were then placed in an oven controlled to be 60℃ for 24h and 105℃ for another 24h for aging of the gel.

6.2.3. Evaluation of the wood-inorganic composites

The pH of the reaction mediums for preparation of the Na_2O-SiO_2 wood-inorganic composites was measured with the pH meter (HORIBA D-13) at 20℃.

The weight percent gain (WPG) and bulking coefficient (B) of the composites were determined by the same procedure described in Chapter 1 and 2, respectively.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were made on the composites by the same procedure described in Chapter 1.

For studying the morphological changes of the composite specimens by heating, samples were treated by thermogravimetric analyzer at 300℃, 450℃ and 650℃. The obtained samples were then studied with a scanning electron microscope (SEM) (JEOL JSM-T330A) at an accelerating voltage of 10 kV.

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

6.3 RESULTS AND DISCUSSION

6.3.1 Na_2O-SiO_2 wood-inorganic composites

Table 6-1 shows the WPG and B for the obtained Na_2O-SiO_2 wood-inorganic composites with sodiummethoxide (SM) or sodiumacetate (SA). The WPGs of these composites were found to be above 20.0 WPG. On the other hand, the B of the composites with SA was higher than that of the composites with SM. These results suggest that in the composites with SA, a larger amount of inorganic gel was formed in the cell walls than in the cell lumens, compared with the composites with SM.

Table 6-1. WPG and B for the prepared Na_2O-SiO_2 wood-inorganic composites.

	Molar ratio						
Composites	MTMOS	MeOH	AcOH	SM	SA	WPG(%)	B(%)
SiO_2	0.03	1	0.01	0	0	11.0	6.6
Na_2O-SiO_2	0.03	1	0.01	0.015	0	27.5	1.3
with SM	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_2O-SiO_2	0.03	1	0.01	0	0.015	24.7	2.5
with SA	0.03	1	0.01	0	0.030	21.3	5.6
	0.03	1	0.01	0	0.060	32.5	8.5

For these composites, SEM observations were, therefore, made and the results were shown in Fig. 6-1. Just for comparison, the result of untreated wood (a) was also shown in the figure. In the composites with SM (b), the inorganic gel was found to be deposited in the cell lumens as shown by the arrows. However, in the composites with SA (c), the inorganic gel could not be observed in the cell lumens as in the untreated wood. The most of the inorganic gel is considered to be formed in the cell walls in the composites with SA. These results of SEM observations could ensure the implication mentioned above. In previous papers (Saka, Sasaki and Tanahashi 1992, Ogiso and Saka 1993, Saka and Yakake 1993), it was revealed that compared with the inorganic gel formed in the cell lumens, the gel within the cell walls was more effective for property-enhancement of wood with a small WPG of the gel. Therefore, the Na_2O-SiO_2 composites prepared with SA are more preferable to enhance the fire-resistance of wood.

6.3.2 Thermal properties of the Na_2O-SiO_2 wood-inorganic composites

Figure 6-2 shows the results of the thermogravimetric (TG) analysis on the Na_2O-SiO_2 composites with SM. For comparisons, the TG curves of the untreated wood and SiO_2 composites are also shown. In the TG curve of untreated wood, an abrupt decrease in its weight by flaming is observed between 300℃ and 350℃. Subsequently, another characteristic decrease in its weight by glowing is also observed between 350℃ and 470℃. Compared with this, the TG curves of the Na_2O-SiO_2 composites are shifted to the lower temperature in their first abrupt decrease for flaming. In addition, between 300℃ and 600℃, the greater residues are resulted after flaming, with a gradual decrease down to about 50% of their original weights. Above 600℃, the TG curves of these composites show an abrupt decrease by glowing. However, the TG curves for this decrease shifted to the higher temperature with an increase in the SM addition to the reaction medium.

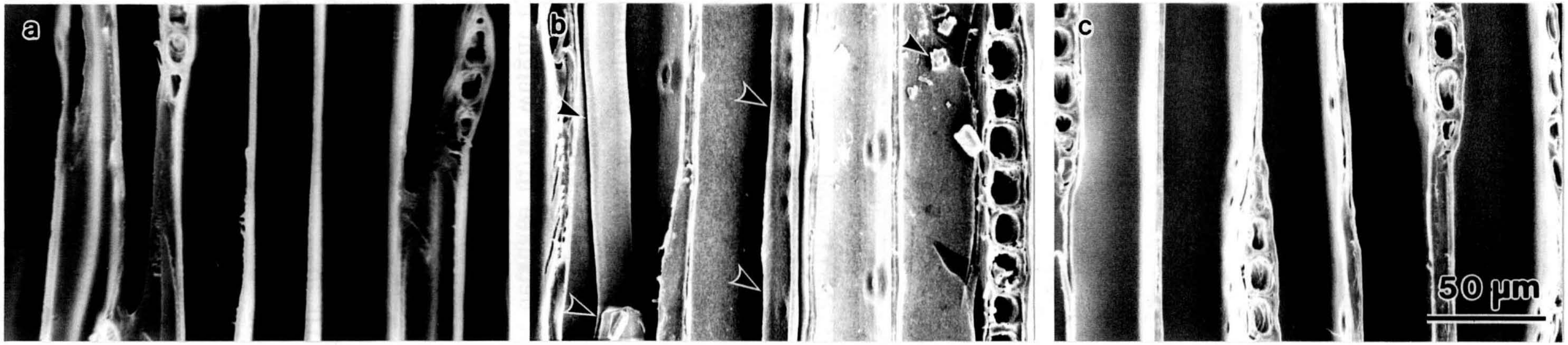


Fig. 6-1. Comparisons of SEM micrographs of untreated wood (a), Na_2O-SiO_2 composites with SM (MTMOS/SM=0.03/0.03, 29.1 WPG) (b) and Na_2O-SiO_2 composites with SA (MTMOS/SA=0.03/0.03, 21.2 WPG) (c).

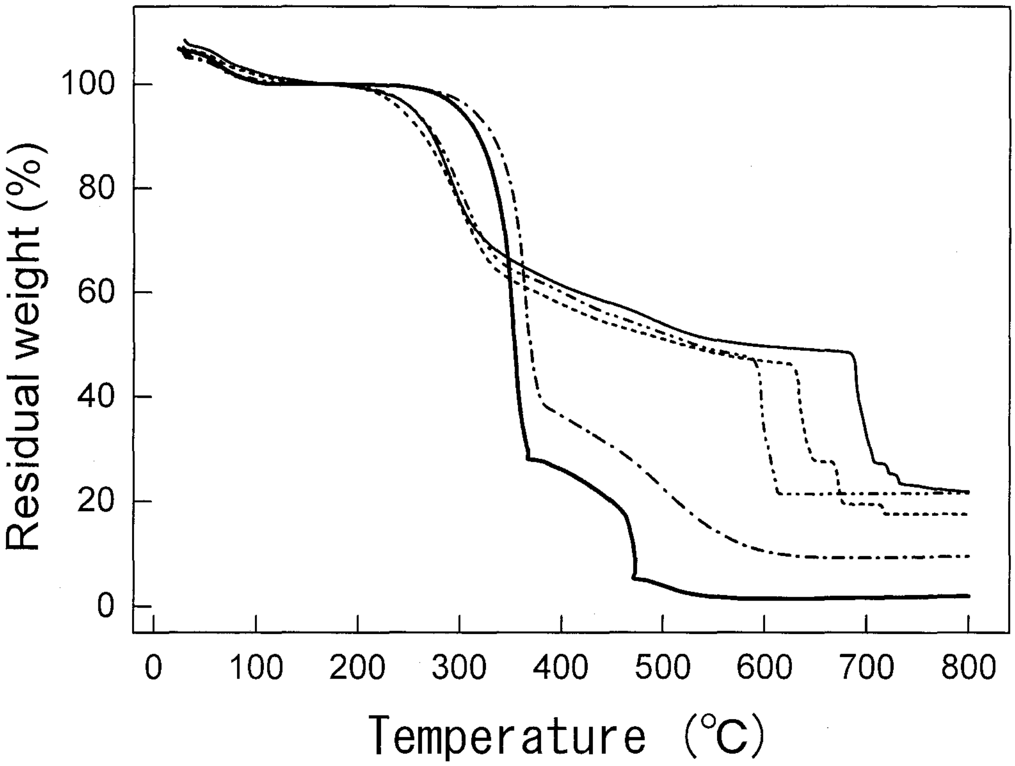


Fig. 6-2. TG curves for the Na_2O-SiO_2 wood-inorganic composites with SM.

—— Untreated

-·-·-· SiO_2 composites (11.0 WPG)

—··—· Na_2O-SiO_2 composites (MTMOS/SM=0.03/0.015, 30.2 WPG)

- - - - - Na_2O-SiO_2 composites (MTMOS/SM=0.03/0.030, 27.6 WPG)

—— Na_2O-SiO_2 composites (MTMOS/SM=0.03/0.060, 26.0 WPG)

Figure 6-3 shows the results of the differential thermal analysis (DTA) for the Na_2O-SiO_2 composites with SM, compared with the untreated wood and SiO_2 composites. The prominent exothermic peaks for flaming and glowing are observed respectively at 360℃ and 440℃ in the DTA of the untreated wood. In the SiO_2 composites, these prominent peaks were weakened and broadened, indicating some fire-resisting properties enhanced. In the Na_2O-SiO_2 composites, however, the exothermic peak for flaming was weakened furthermore with shifting its peak to the lower temperature, and only broad exothermic peak hill is observed at about 300℃. These results indicated the enhanced fire-resistance for flaming in the Na_2O-SiO_2

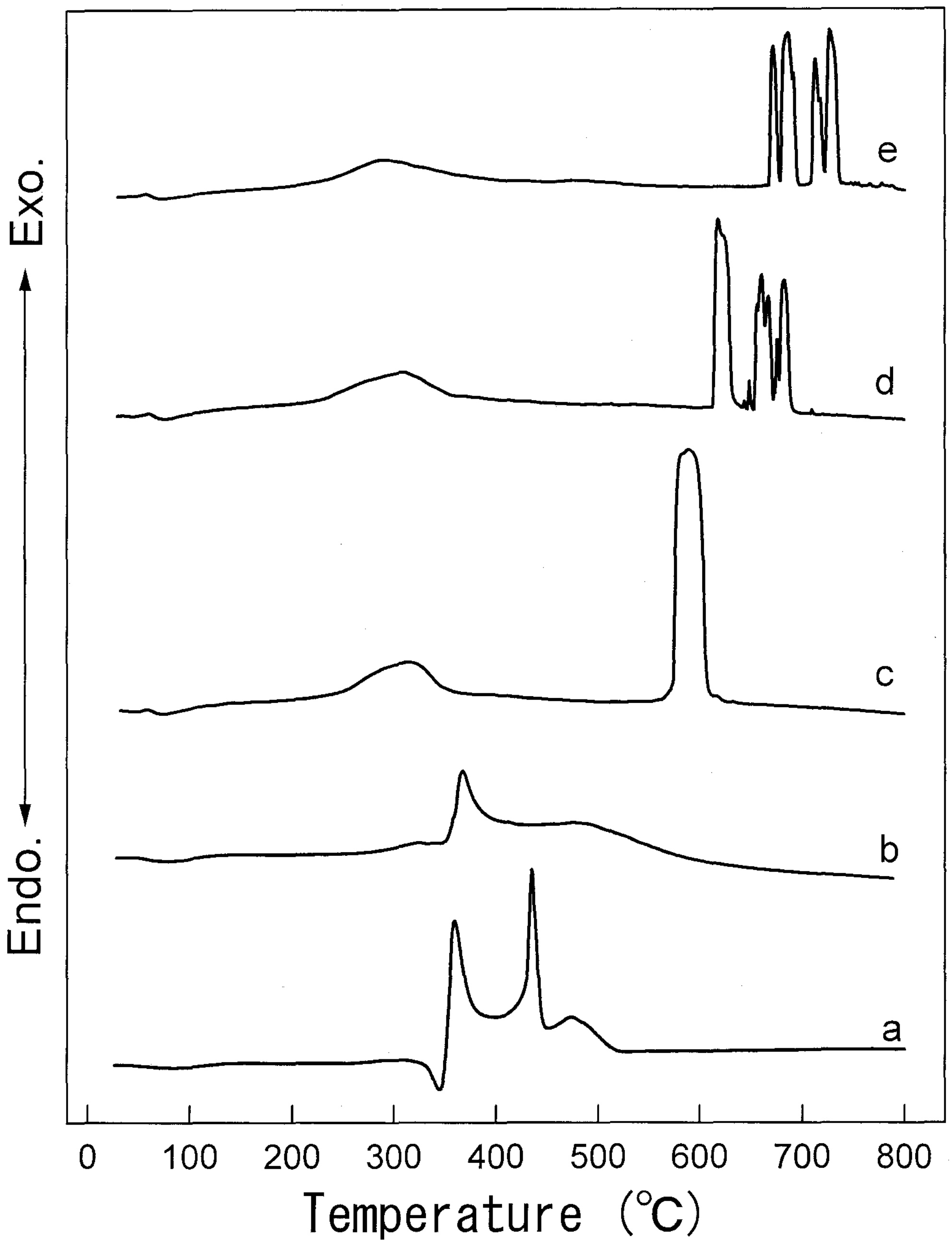


Fig. 6-3. DTA curves for the Na_2O-SiO_2 wood-inorganic composites with SM.
(a) Untreated (b) SiO_2 composites (11.0 WPG)
(c) Na_2O-SiO_2 composites (MTMOS/SM=0.03/0.015, 30.2 WPG)
(d) Na_2O-SiO_2 composites (MTMOS/SM=0.03/0.030, 27.6 WPG)
(e) Na_2O-SiO_2 composites (MTMOS/SM=0.03/0.060, 26.0 WPG)

composites. In the DTA curves of the Na_2O-SiO_2 composites at the higher temperature over 600℃, the prominent peaks are observed, which are due to the glowing. In addition, the peak temperature was shifted to the higher temperature with an increase in the SM addition to the reaction medium. This shift corresponds to that of the temperature of the abrupt weight decrease in the TG curves as shown in Fig. 6-2.

From these results, it was considered that the Na_2O-SiO_2 composites can raise the glowing temperature, in spite of its exothermic behaviors occurred. In particular, the composites prepared from the reaction medium with a molar ratio of 0.060:0.03 in SM and MTMOS could surprisingly raise the glowing temperature up to about 700℃.

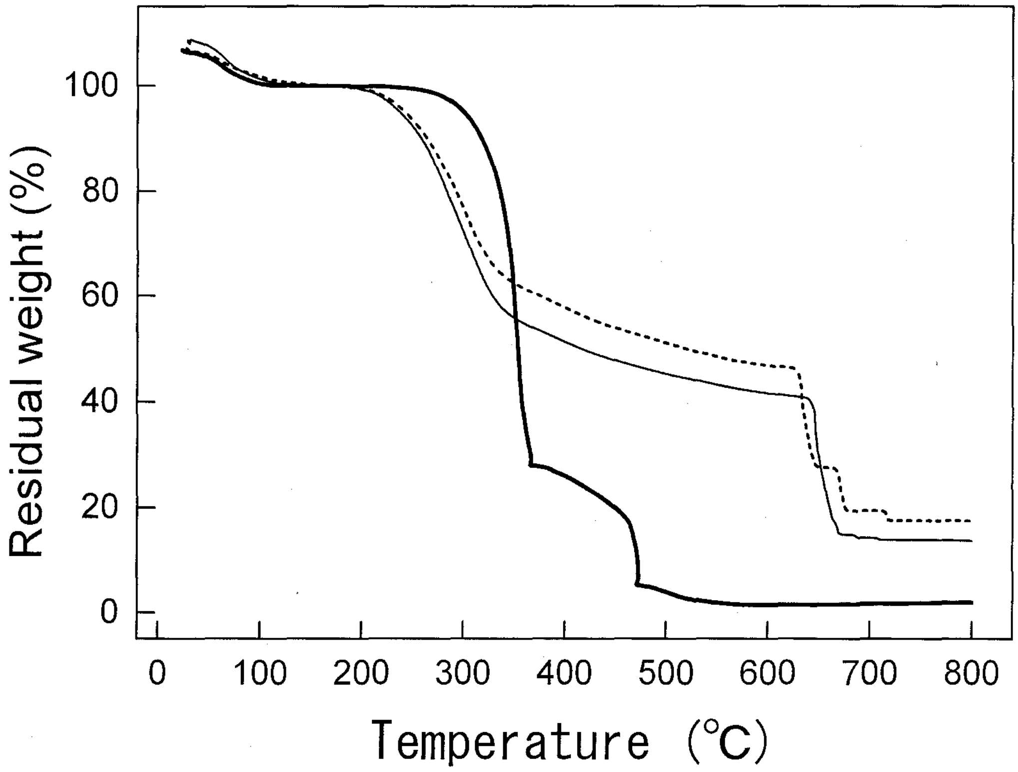


Fig. 6-4. TG curves for the Na_2O-SiO_2 wood-inorganic composites with SA.
——— Untreated
- - - - - Na_2O-SiO_2 composites with SM (MTMOS/SM=0.03/0.03, 27.6 WPG)
——— Na_2O-SiO_2 composites with SA (MTMOS/SA=0.03/0.03, 21.2 WPG)

Figure 6-4 shows the results of the TG analysis for the Na_2O-SiO_2 wood-inorganic composites with SA. For comparisons, the TG curves of the untreated wood and the Na_2O-SiO_2 composites with SM are also shown. Compared with the untreated wood, the TG curve of the Na_2O-SiO_2 composites with SA is shifted to the lower temperature for flaming. In addition, between 300℃ and 600℃, the greater residues are resulted after flaming. As a result, the glowing temperature is raised up to about 600℃ as observed in the composites with SM. However, a closer inspection indicates that the Na_2O-SiO_2 composites with SA are lower in its residual weight after flaming, compared with the composites with SM. However, considering the difference of the WPGs in these composites, the fire-resisting effect of these composites can be assumed to be essentially the same.

Figure 6-5 shows the results of the DTA for the Na_2O-SiO_2 composites with SA, compared with the untreated wood and the Na_2O-SiO_2 composites with SM. The prominent exothermic peak observed in the untreated wood for flaming is weakened and peak for glowing is shifted to the higher temperature of about 650℃, as seen in composites with SM. From these results, it is obvious that the Na_2O-SiO_2 composites with SA have a great fire-resisting effects as observed in the Na_2O-SiO_2 composites with SM.

Such results of the enhanced fire-resistance of the Na_2O-SiO_2 composites are ensured in Fig. 6-6 which shows the results of the fire-resisting tests. The untreated specimens became shorter with ashes due to combustion. Compared with this, the SiO_2 composites revealed some fire-resistance with the longer carbonized residue. However, Na_2O-SiO_2 composites revealed much greater resistance against burning with longer but less carbonized residue.

6.3.3 Mechanisms of fire-resistance of the Na_2O-SiO_2 composites

In Chapters 3 and 4, the TG curves for flaming in the binary SiO_2-P_2O_5 composites were found to be shifted to the lower temperature, compared with

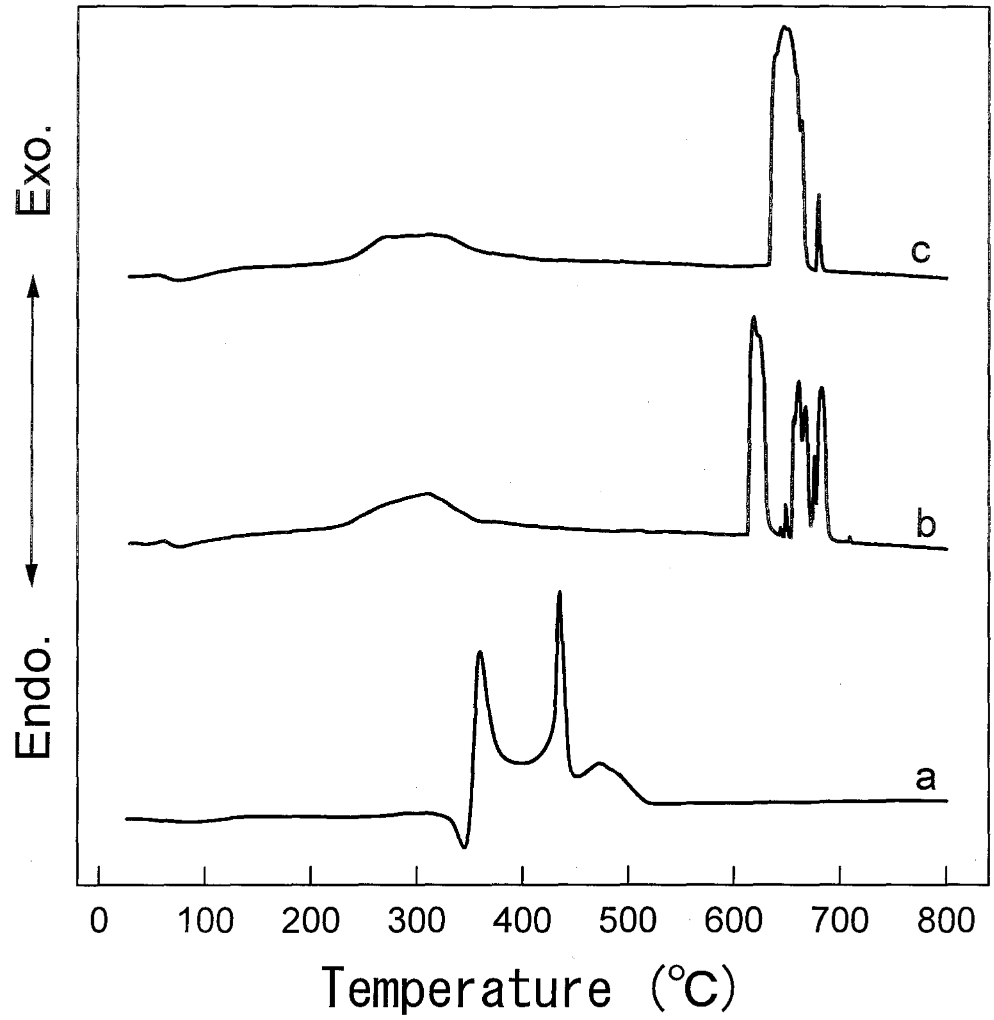


Fig. 6-5. DTA curves for the Na_2O-SiO_2 wood-inorganic composites with SA.
(a) Untreated
(b) Na_2O-SiO_2 composites with SM (MTMOS/SM=0.03/0.03, 27.6 WPG)
(c) Na_2O-SiO_2 composites with SA (MTMOS/SA=0.03/0.03, 21.2 WPG)

that in the untreated wood. This was due to the enhanced dehydration reaction with the phosphorous compound. Basic sodium compound is also known to have a similar effect to the phosphorous compound (Browne 1958). Due to this chemical effect, TG curves for flaming in the binary Na_2O-SiO_2 composites would be shifted to the lower temperature as in Figs. 6-2 and 6-4, and thus these composites could have attained the enhanced fire-resistance for flaming.

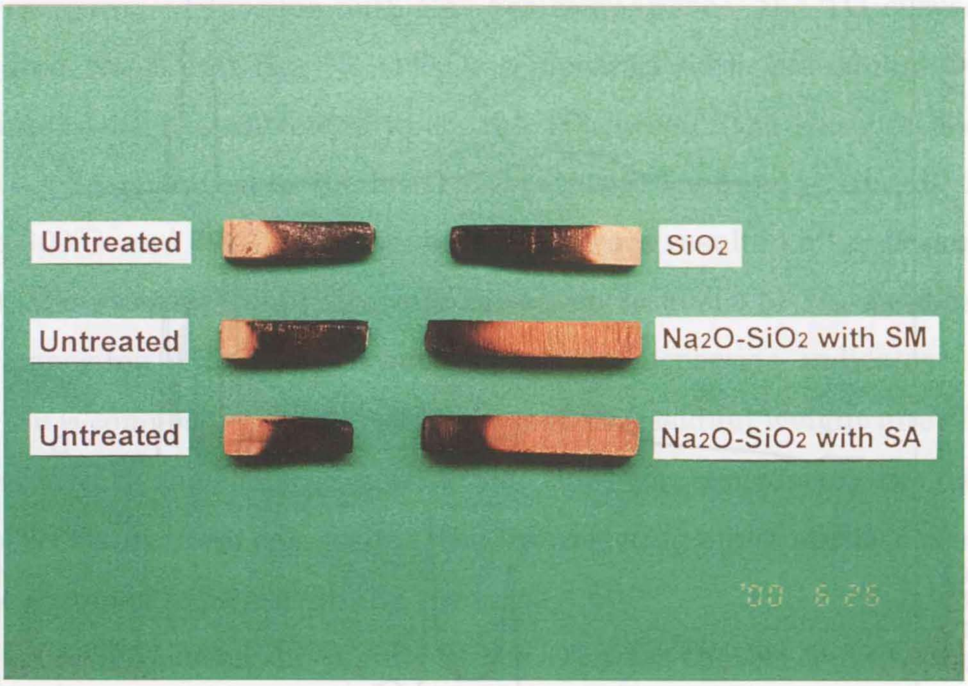


Fig. 6-6. Comparison of burned specimens after the fire-resisting test. Untreated wood specimens (left) *vs.* SiO_2, Na_2O-SiO_2 wood-inorganic composites with SM and Na_2O-SiO_2 wood-inorganic composites with SA.

To clarify the mechanisms of fire-resistance of the Na_2O-SiO_2 composites for glowing, SEM observations were made on the composites treated at 300℃, 450℃ and 650℃ as shown in Fig. 6-7. Although some inorganic gel can be seen on the surface of the cell walls in the composites at room temperature (a), those were not observed in the composites treated at 300℃ and 450℃ ((b) and (c)). However, at 650℃ ((d) and (e)), these components can be seen again on the surfaces of the cell walls. From these results, it is assumed that the gel formed in wood would have melted and covered over the surfaces of wood cells with glassy layers as the temperature was raised. This glassy layer could have prevented the cell wall components from being volatile products of combustion and further being exposed with oxygen. Therefore, the fire-resistance for glowing could be achieved successfully. However, as the

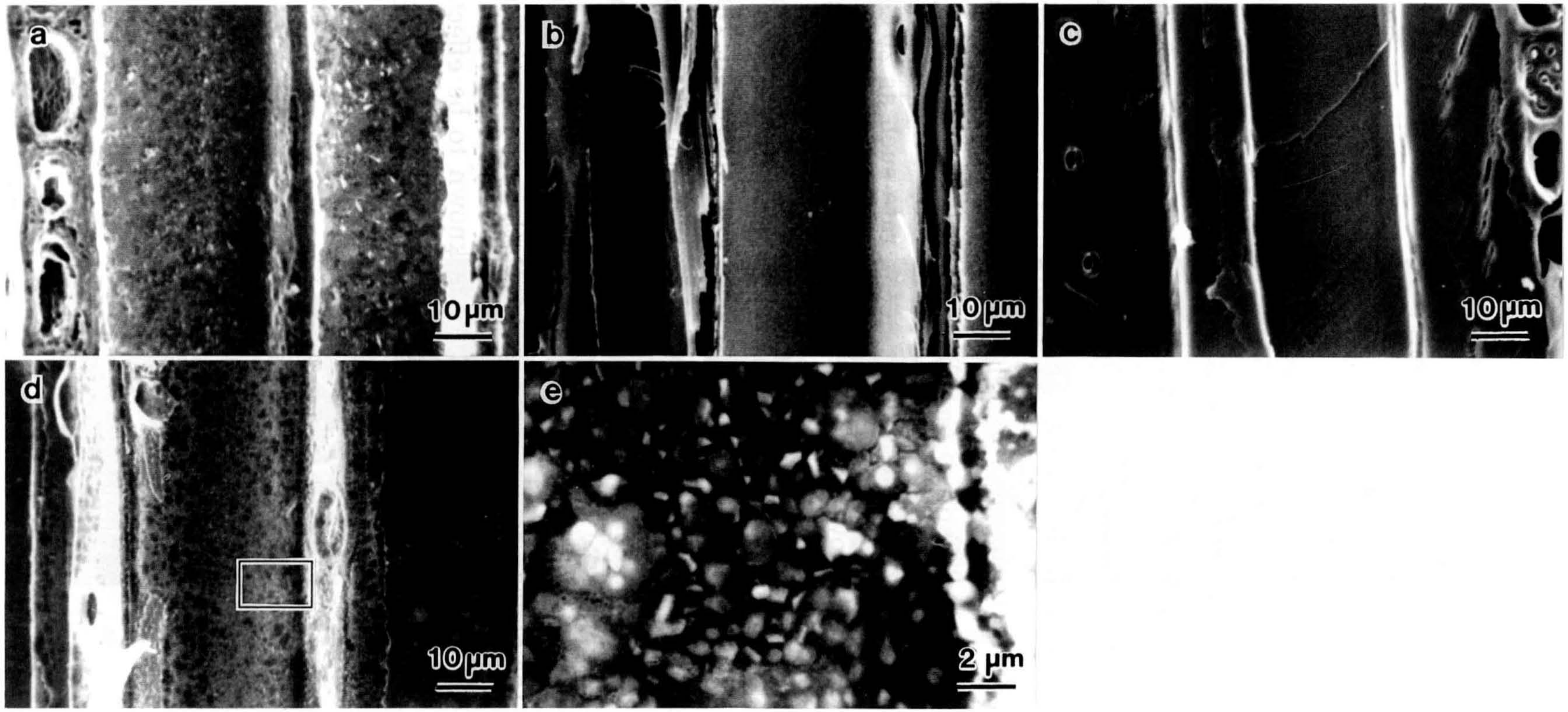


Fig. 6-7. Comparisons among the Na_2O-SiO_2 wood-inorganic composites with SM (MTMOS/SM=0.03/0.06, 26.0 WPG) treated at various temperatures.
(a) Room temperature (b) 300℃ (c) 450℃ (d) 650℃ (e) Magnified view of (d).

temperature was raised further, the glassy layer shrank to the granules as in Fig. 6-7(e). With this shrinkage of the glassy layer covered over the cell walls, oxygen would be accessed to the cell wall components of wood and the glowing would subsequently occur.

To study morphological changes further, more intensive SEM observations were made on the composites after fire-resisting tests and compared with untreated wood as in Fig. 6-8. The Na_2O-SiO_2 composites were found to form an intumecent structure over the surfaces of the cell walls which would not be observed in the untreated wood. This intumecent structure was not, however, observed in the composites treated by thermogravimetric analyzer, as shown in Fig. 6-7. This difference may be due to the heating rate. When the Na_2O-SiO_2 composites treated at lower heating rate such as 20℃/min, a variety of reactions occur slowly during the process of heating such as dehydration of wood by Na_2O gel, vaporization of some volatile compounds, melting of the gel and forming of the glassy layer over the wood. However, with the rapid heating as happened in a exposure of flame, these reactions would take place instantaneously and vigorously. Therefore, intumecent structure over the surfaces of the cell walls in the Na_2O-SiO_2 composites could be formed by the glazing of the melted gel with the vaporization of some volatile compounds. Such intumecent structure is known to be effective for enhancing the fire-resisting properties with insulating the wood (Browne 1958, Vandersall 1971). The Na_2O-SiO_2 composites, therefore, could attain their enhanced fire-resistance as in fire-resisting tests not only by the coating effects of glassy layer mentioned above but also by the insulating effects of an intumecent structure formed over the surfaces of the wood cell walls in the composites.

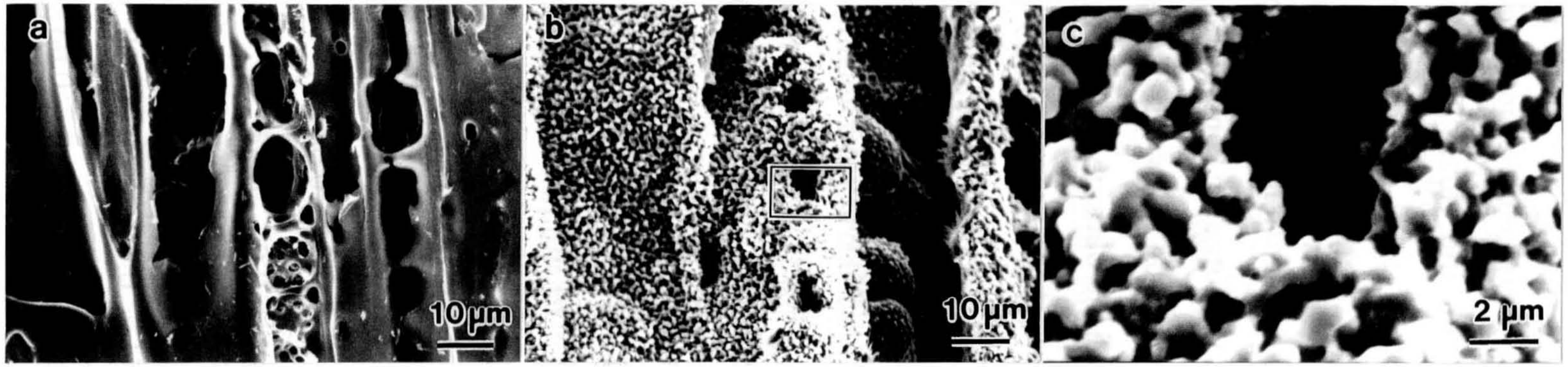


Fig. 6-8. Comparisons between the Na_2O-SiO_2 wood-inorganic composites with SM and untreated wood after fire-resisting tests.
(a) Untreated wood (b) Na_2O-SiO_2 wood-inorganic composites (c) Magnified view of (b).

6.3.4 The pH of the reaction mediums for the Na_2O-SiO_2 wood-inorganic composites

Table 6-2 shows the pH of the reaction mediums for the Na_2O-SiO_2 composites with SM and SA (No.1 and No.3). The molar ratio of the chemical components is also shown in the table. Although a reaction medium with SM (No.1) is basic, a reaction medium with SA (No.3) is weakly acidic. During the impregnation of these reaction mediums into the moisture-conditioned wood to obtain the Na_2O-SiO_2 wood-inorganic composites, these reaction mediums 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 6-2 (No.2 and No.4). It was consequently found that No.1 solution becomes strong in its basicity by the addition of water, whereas the pH of No.4 solution remains almost unchanged with weak acidity. In a report about the alkaline strain on wood (Takenami 1965), the discoloration became remarkable by the basic treatment of the solution over about 11 at pH. Therefore, a reaction medium for the Na_2O-SiO_2 composites with SM would

Table 6-2. The pH of the reaction mediums for the Na_2O-SiO_2 wood-inorganic composites.

	Molar ratio						
No.	MTMOS	MeOH	AcOH	SM	SA	H_2O	pH
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

possibly cause the discoloration during the impregnation treatment. Based on these lines of evidence, the reaction medium with SA is practically preferable for preparing the Na_2O-SiO_2 composites, compared with that with SM.

6.4 SUMMARY

For enhancing the fire-resisting properties, a binary system to prepare wood-inorganic composites was studied by adding SM or SA to a reaction system for SiO_2 composites. Compared with the SiO_2 composites, the obtained Na_2O-SiO_2 composites could be improved greatly in the fire-resisting properties of wood. From the SEM observation, this enhanced fire-resistance was assumed to be due to the chemical and physico-chemical effects such as the dehydration and carbonization of wood by Na_2O gel, the glassy layer and intumecent structure formed over the cell walls which were considered to prevent oxidation and heat transfer from proceeding into the inner portion of the wood cell walls. However, the Na_2O-SiO_2 composites with SM may have a problem in the degradation of wood due to the treatment with a basic reaction medium. Additionally, in the Na_2O-SiO_2 composites with SA, the inorganic gel was formed only within the cell wall with retaining the structure characteristic of wood. Therefore, the application of SA is preferable to that of SM for preparing the Na_2O-SiO_2 composites with high fire-resistance.

Conclusions

Although wood is a super natural composite material, it has some unfavorable end-products properties in dimensional stability, combustibility, and biodeterioration. In this dissertation, to improve and enhance the properties of wood particularly in fire-resistance, sol-gel method was applied to prepare the wood-inorganic composites.

In Chapter 1, various wood-inorganic composites were prepared from various metal alkoxides in mono-reaction systems and studied on their thermal properties by TGA and DTA. In the TG curves of the SiO_2, P_2O_5 and B_2O_3 composites, the higher residue after flaming and gradual decrease during their glowing could be seen, compared with the untreated wood. In the DTA curves of SiO_2, P_2O_5 and B_2O_3 composites, the prominent exothermic peaks for flaming and glowing as shown in untreated wood were not observed. From these results, it is revealed that the SiO_2, P_2O_5, and B_2O_3 composites can have a good fire-resistance with a small WPG.

In Chapter 2, various titanium alkoxides or titanium chelates were used for preparing TiO_2 wood-inorganic composites. From SEM-EDXA analyses on the obtained composites, in the TiO_2 composites from titanium alkoxides or titanium chelates which have the lower rate of hydrolysis and subsequent polycondensation, the TiO_2 gel were found to distribute only within the cell walls. It was also found that the TiO_2 gel deposited within the cell walls could improve the properties of wood in dimensional stability and fire-resistance, whereas for the gels in the cell lumens, property enhancement could not be achieved. From these results, the topochemical effect of TiO_2 gel exists for enhancement of properties in wood-inorganic composites, as observed in SiO_2 wood-inorganic composites.

In Chapter 3, trimethylphosphite (TMP) and/or trimethylborate (TMB) were applied to a reaction system for SiO_2 composites to prepare the binary

SiO_2-P_2O_5, SiO_2-B_2O_3 and ternary SiO_2-P_2O_5-B_2O_3 wood-inorganic composites for enhancing the fire-resisting properties of wood furthermore. The obtained composites were studied on their thermal properties. It is, consequently, revealed that these composites have high fire-resistance, compared with the untreated wood and SiO_2 composites, while keeping more or less the porous structure characteristic of wood. The effects of the SiO_2, P_2O_5 and B_2O_3 gels on the thermal properties of wood were also studied. The fire-resisting effects of the composites in binary or ternary reaction systems may be due to the physical effects such as glassy layer by the SiO_2 and B_2O_3 gels over the surface of the cell wall, and chemical effects such as dehydration of the cell wall components by the P_2O_5 gel.

However, SiO_2-P_2O_5-B_2O_3 composites in binary and ternary reaction systems have the problems in the stability of P_2O_5 and B_2O_3 gels against the weathering, and the odor and harm problems of chemicals in TMP and TMB. To overcome these problems, in Chapter 4, some silicon alkoxide oligomers with phosphorous and/or boric hydroxide residues were prepared and applied to prepare the SiO_2-P_2O_5-B_2O_3 wood-inorganic composites from oligomers. The obtained composites were found to have an enhanced fire-resistance and prevent the gel from leaching. Additionally, the prepared oligomers are non-toxic so that the environmental safety for preparation was achieved. To improve the stability of the P_2O_5 and B_2O_3 gels furthermore by enhancing the water-repellent properties of the composites, 2-heptadecafluorooctylethyl-trimethoxysilane (HFOETMOS) was applied to oligomer reaction system. The obtained composites could achieve higher anti-leachability of the gel.

In Chapter 5, to elucidate the mechanism for enhancing the water-repellent property by HFOETMOS, the HFOETMOS-SiO_2 wood-inorganic composites with various WPGs were prepared and studied on their water-repellent properties. The obtained composites with the lower WPG have attained the high water-repellency, though those with the higher

WPG could not revealed good property in water-repellency. From the SEM-EDXA analysis on these composites, it was assumed that the cell wall in the composites with lower WPG would be covered with the long hydrophobic perfluoro alkyl residue of the HFOETMOS, whereas for the composites with higher WPG, SiO_2 gel formed in the cell lumen would have prevented HFOETMOS-derived residues from being exposed uniformly over the surface of cell wall. From these results, for enhancing the water-repellency, it is significant to distribute HFOETMOS molecules with the long hydrophobic perfluoro alkyl chain over the surface of cell walls uniformly. This suggests that the topochemical effect of HOETMOS molecules exists for enhancement of properties in wood-inorganic composites.

In Chapter 6, as next trials, sodium methoxide (SM) or sodium acetate (SA) was applied to a reaction system for SiO_2 composites to prepare the binary Na_2O-SiO_2 wood-inorganic composites for enhancing the fire-resistance of wood furthermore. The prepared Na_2O-SiO_2 composites were found to have enhanced fire-resistance with greater residue at high temperature over 600℃, compared with the SiO_2 composites. From the SEM observations, the fire-resistance of the Na_2O-SiO_2 composites may be due to the chemical and physico-chemical effects such as the dehydration and carbonization of wood by Na_2O gel, the glassy layer and intumecent structure formed over the cell walls which were considered to prevent oxidation and heat transfer from proceeding into the inner portion of the wood cell walls. However, reaction medium for the Na_2O-SiO_2 composites with SM may cause the degradation of wood due to its basicity. Additionally, the Na_2O-SiO_2 composites with SA can retain the porous structure of wood without forming the inorganic gel in the cell lumens. Therefore, it is better to use SA for preparing the Na_2O-SiO_2 composites with high fire-resistance.

Consequently, the mechanisms of the fire-resistance for several wood-inorganic composites prepared were summarized as in Fig. 7-1.

Although these mechanisms were proposed in a previous study on the fire-resistance of wood (Browne 1958), these were thought to be available for this study. Due to these physical and chemical effects, wood-inorganic composites prepared in this study can prevent the flaming or glowing and attain the high fire-resistance.

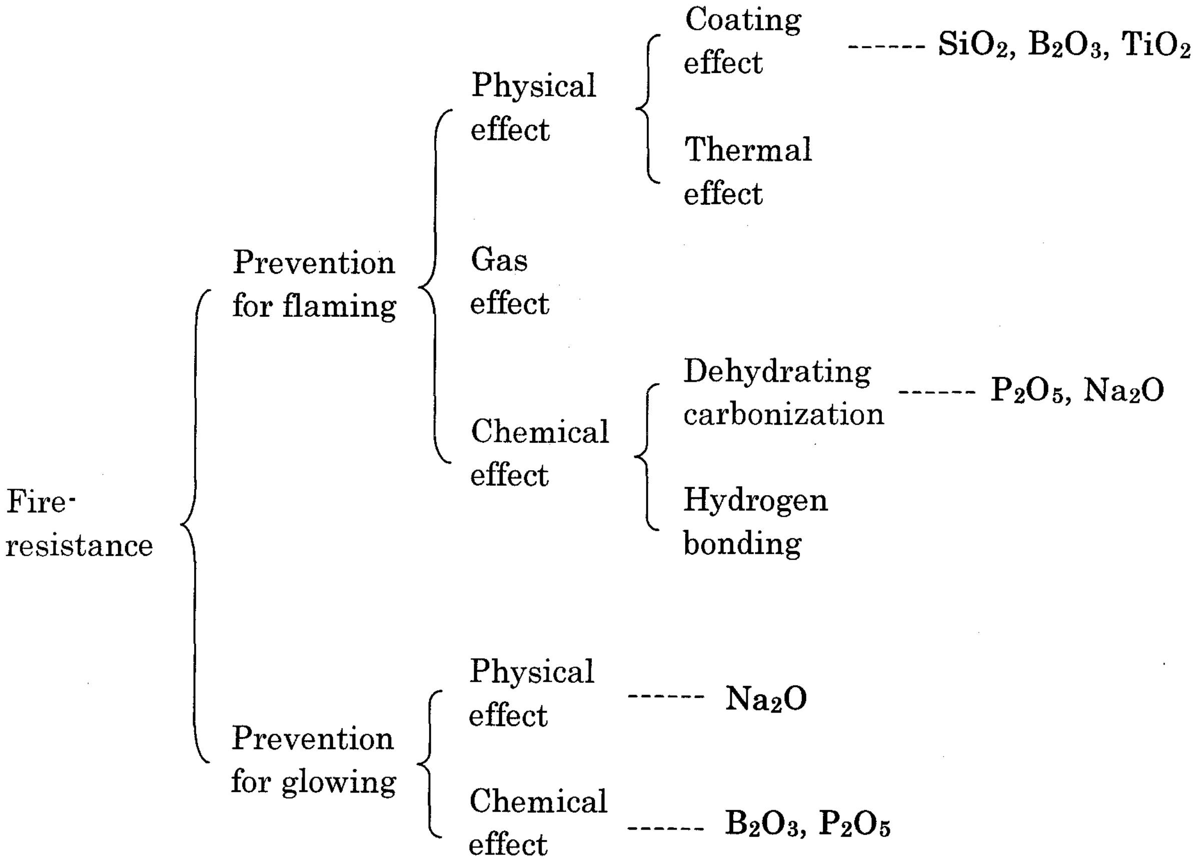


Fig. 7-1. Mechanisms for fire-resistance.

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