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Improvement of fire retardancy of plywood by incorporating boron or phosphate compounds in the glue*

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Abstract A practical approach to enhancing the fire retardancy of wood-based materials by adding fire-retardant chemicals to the glue was developed. Plywoods were manufactured using urea melamine formaldehyde resin mixed with ammonium pentaborate or dihydrogen phosphate. Treated plywoods had better incombustibility than untreated ones. X-ray photoelectron spectroscopy (XPS) analysis clearly demonstrated the distribution of boron and phosphorus, which had migrated from the glue to the wood, contributing to better fire retardant properties. The cross-sectional micrographs from scanning electron microscopy showed that untreated specimens exhibited a foamy structure near the interface in the glue layer and the deformed structure of wood cells. The cell structure and cell wall thickness retained intact in the specimens treated with urea melamine formaldehyde resin mixed with ammonium pentaborate or dihydrogen phosphate. When observing the effect of the thickness of overlay veneers on incombustibility, a shorter glowing time was obtained from the specimens with a thicker surface layer when the fire retardant chemical was added at 2%, but the differences were smaller at the higher chemical retention of 4%. A similar tendency was observed for the char length.

Key words Fire retardancy · Plywood · Glue-additive treatment · Char length · XPS

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Introduction

Wood is the preferred material for residential construction, although its combustibility is one of its unfavorable properties, especially when used for partition walls. In our previous studies on strandboard and plywood, coating the surface with urea melamine resin that included the fire retardant boron or phosphorus compound was found to be an economical method to provide them with effective fire retardant properties.^{1,2} The wood-based materials in which urea melamine with fire retardants was distributed in the surface layer had enhanced incombustibility and unleachability. A treatment that uses the adhesive plus preservatives is thought to be another way to provide higher endurance performance to wood-based materials.

Meranti plywoods treated with the glue-additive method were developed using wood preservative chemicals, and long-term usage improved to a certain degree.³ This performance, however, changed depending on the variety of fungi to which the plywood was exposed and the weathering procedure conducted before testing in this study. It was also observed that the biological resistance of particleboard using susceptible albizzia wood as the raw material was enhanced by incorporating fungicides and insecticides into the adhesives.⁴ Fungicide treatment of particleboards was found to inhibit fungal deterioration and prevent termite attacks. The glue-additive treatment was also introduced to the production of incombustible plywood, and it was reported that its flammatory property was suppressed by mixing polyphosphate carbonate in the urea resin.⁵ The thickness of the veneer was said to influence the effectiveness of plywood when treated with the glue-additive method and so should be considered for a reliable manufacturing process as well as to enhance the bonding qualities.⁶

The chemicals added in the glue were believed to penetrate the wood materials during hot-pressing, contributing to upgrading the properties.⁷ Little information, however, has been obtained regarding the relation between the penetration or distribution of preservatives and the performance of the materials, although preservatives have been

assumed to be important for its effectiveness. It was therefore necessary to study systematically the glue-additive method as it is applied in the industry.

In the present study, boron and phosphorus compounds were added to the glue to enhance the fire resistant properties of plywood. Their incombustible properties were evaluated by a JIS standard method. To investigate the penetration of chemical elements into wood, the migration of boron or phosphorus elements was analyzed by means of X-ray photoelectron spectroscopy and scanning electron microscopy at the submicro and ultramicro levels.

Materials and methods

Materials

Veneers of radiata pine (*Pinus radiata*) (original thickness 2.6 mm) and port orford cedar (*Chamaecyparis lawsoniana*) (0.3- and 0.6-mm thicknesses) were cut into 30 × 15 cm blocks. The average air-dried moisture content before the manufacture of plywood was 9.5%.

Fire-retardant chemical incorporation into glue

Commercially produced urea melamine formaldehyde resin (UM-85; Aica Industries, Aichi, Japan) was the adhesives used in the manufacture of plywood; 250 g/m² was applied. The urea melamine formaldehyde resin had a solid content at 52% and a gel time of 37 min at 50°C. The viscosity was 0.31 Pa·s and the pH 9.0 at 23°C.

The urea melamine formaldehyde resin (UM) was mixed with ammonium pentaborate, (NH₄)₂·5B₂O₃·8H₂O, abbreviated as UMB. The addition ratios were adjusted to 2% and 4% based on the boron/urea melamine formaldehyde resin molecular weight ratio. Ammonium dihydrogen phosphate (NH₄H₂PO₄) (UMP) was used instead of ammonium pentaborate in some cases, with the addition ratios adjusted to 2%, 4%, and 6% based on the phosphorus/urea melamine formaldehyde resin molecular weight ratio.

Port orford cedar was used as the surface layer for three-ply plywood. The veneers of radiata pine were coated on one surface with normal glue or fire retardant glue at a specified amount and used as the core and bottom layers of the plywood. The glue-coated veneers were cold-pressed for 30 min and then hot-pressed at 120°C with a pressure of about 785 kPa for 6 min to cure the resin.

Incombustibility test

The untreated and fire-retardant-chemical-treated plywoods were tested according to JIS A 1322 (testing method for incombustibility of thin materials for buildings).⁸ The specimens were dried at a temperature of 50° ± 2°C for 48 h and left in a desiccator with silica gel for 24 h. The specimens were then clamped with a steel holder and kept steady at the heating flame at an angle of 45 degrees. The heating

flame, adjusted to a length of 65 mm from the bottom, was applied for 4.5 min. According to JIS A 1322, the duration of heating by the flame must be set between 10 s and 3 min because this standard evaluates the incombustion properties of materials <5 mm in thickness. In this study, however, the time was adjusted to 4.5 min as the thickness of the specimens was >5 mm. The results obtained in this study hardly meet the criteria described in JIS A 1322 but were compared to evaluate the effects of the glue-additive treatment.

The after-flaming time (i.e., duration of continuous flaming after removing the heating source) was observed. The glowing time (state of nonflame combustion after cessation of the flame) was also recorded. After the test the weight loss of each specimen was measured for comparison with the initial weight. The ratio of weight loss was then calculated, comparing the tested specimens with the untreated ones. The char length of a tested specimen was measured after brushing and removing the charred surface.

Line scan analysis by X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) spectra of the cross section of untreated and 4% UMB- and UMP-treated specimens were obtained by the Shimadzu KRATOS AXIS-HS-1 apparatus using a MgK photon source. The anode voltage was 15 kV and the anode current 10 mA. The background pressure in the analytical chamber was less than 10⁻⁸ mmHg. The line scan was performed under the setting of neutralizer to eliminate the charge effect.

Scanning electron microscope observation

The scanning electron microscope (SEM) micrographs were obtained by the JSM 5310 apparatus. The untreated and 4% UMB- and 4% UMP-treated plywoods were microtomed on the cross section after exposure to the flammability test and coated with gold for SEM observations.

Results and discussion

Effects of chemical treatment on incombustible properties

After-flame was rarely observed in the treated specimens, although plywoods treated with fire retardant chemicals glowed. The duration of the glow was recorded and compared to that of the untreated specimens, as shown in Fig. 1. When the amount of (NH₄)₂O·5B₂O₃·8H₂O added was increased, the glowing time of the UMB-treated specimens was reduced. When the amount added was increased to 2% and 4%, the average glowing times were about 140 s and 60 s, respectively, which showed a marked improvement compared to the untreated specimens, which had a glowing time of more than 600 s. UMP-treated plywood also showed

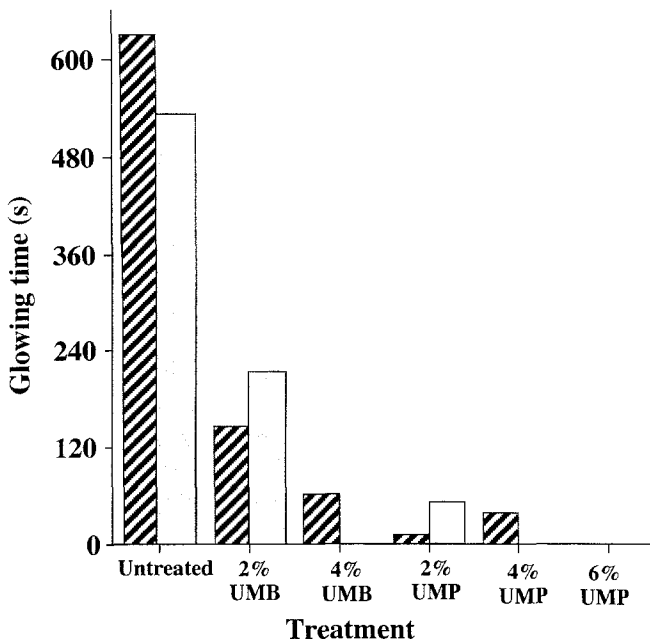


Fig. 1. Relation between treatments and glowing time of plywoods. *UMB*, urea melamine formaldehyde resin + ammonium pentaborate (2%, 4%); *UMP*, urea melamine formaldehyde resin + dihydrogen phosphate (2%, 4%, 6%). Concentrations of added chemicals are based on the molecular weight ratios of boron or phosphorous to resin, respectively. *Cross-hatched bars*, plywood overlaid with 0.6 mm of sliced veneer; *gray bars*, plywood overlaid with 0.3 mm of sliced veneer

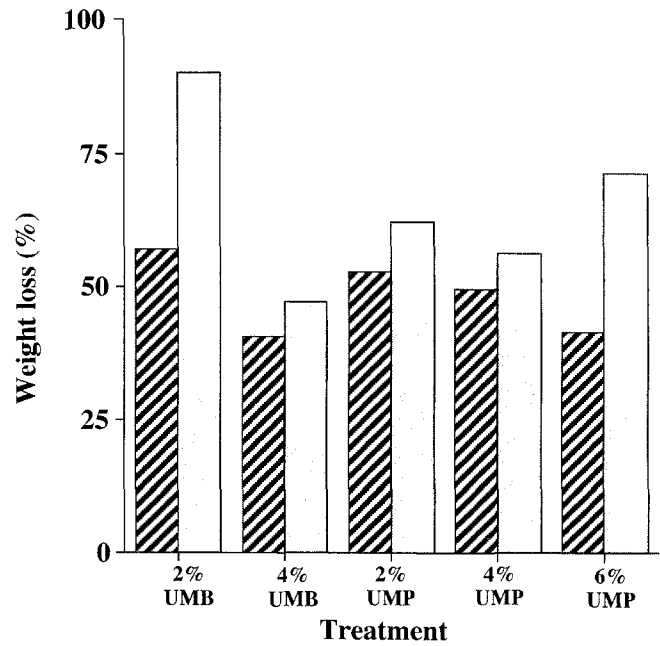


Fig. 2. Relation between treatments and weight loss ratio of plywoods. See Fig. 1 for explanation of symbols

almost total suppression of the glowing time with the 2%, 4%, and 6% additions. Generally, UMP showed better efficiency for reducing the glowing time than did UMB.

Both phosphorus and boron compounds effectively promote the carbonization of treated wood without an outbreak of flame.¹ In this study UMP more efficiently shortened the glowing time, perhaps owing to the effect of synergism between phosphorus and the nitrogen in the resin.

The effect on weight loss is shown in Fig. 2. The weight-loss ratio was reduced in the specimens treated with UMB or UMP, and it was further reduced when the treating amount was increased. It is known that a glassy protection layer of diboron trioxide delays the oxidization of carbon, which is activated on the heat-exposed surface during treatment with UMB.⁹ An additional charred layer was formed on the surface exposed to fire during the treatment with UMP. The UMB-treated specimens experienced weight loss similar to that of the UMP-treated specimens at each concentration, as shown in Fig. 2.

The char lengths of the UMB- and UMP-treated specimens were reduced with an increasing amount of the chemical (Fig. 3). As described in a previous study,¹ the thermal decomposed products that contribute to combustion were mainly released through the cracks formed on the fire-exposed surface of the board. The char length observed in this study reflects the ease with which cracks are formed on the surface of the plywood and the continuous supply of combustion products. Flaming did not occur in either the UMP- or UMB-treated specimens. It is suggested that the

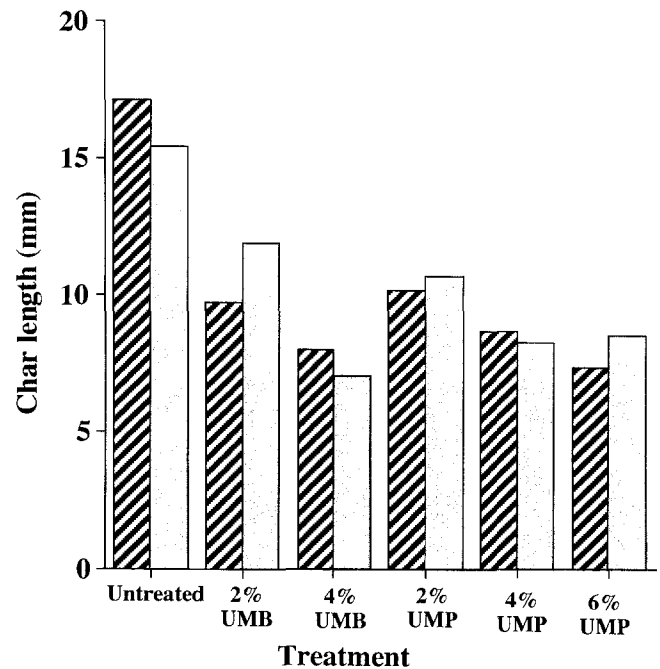


Fig. 3. Relation between treatments and char length of plywoods. See Fig. 1 for explanation of symbols

charred layer that slowly and steadily formed on the surface insulated the heat energy and prevented the inflammable gas coming through the weakly distributed cracks.

Chemical migration observed by line scan analysis of XPS

The distribution of nitrogen, boron, and phosphorus was observed around the glue line region by line-scan analysis of

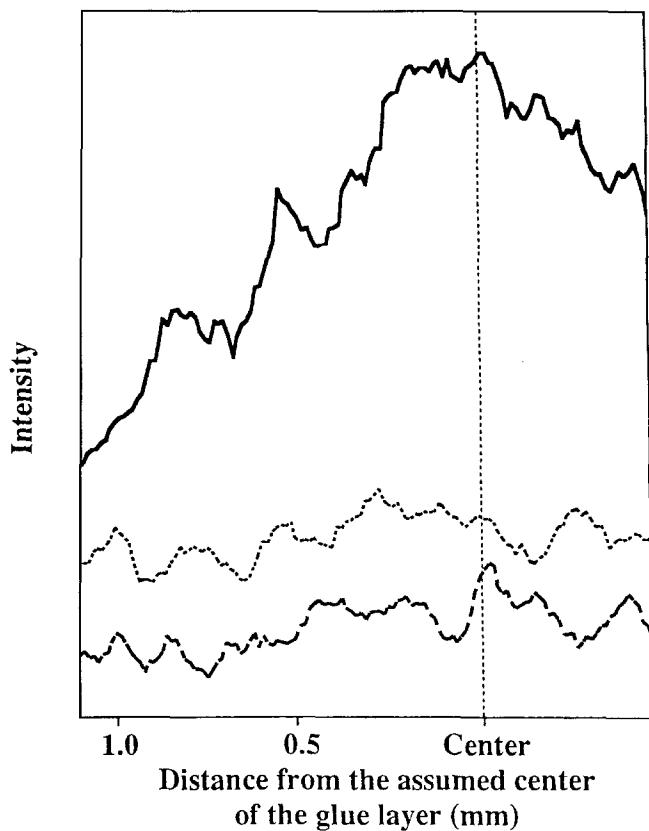


Fig. 4. Intensity of nitrogen, boron, and phosphorus in an untreated specimen. *Solid line*, nitrogen; *dotted line*, boron; *broken line*, phosphorus. No peak was detected for boron or phosphorus in the untreated specimen

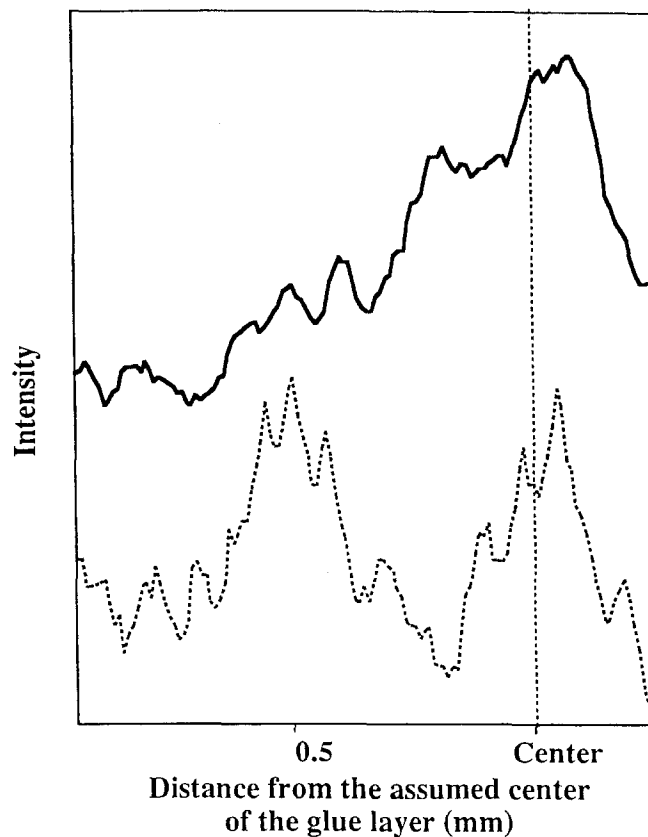


Fig. 5. Intensities of nitrogen and boron in the 4% UMB-treated specimen. *Solid line*, nitrogen; *dotted line*, boron

XPS. As shown in Fig. 4, the untreated plywood displayed an intensified peak of nitrogen around the scan width of about 1.5 mm. The nitrogen peak revealed the presence of the glue where nitrogen was almost symmetrically distributed along the glue line. There were no obvious peaks of boron or phosphorus because these compounds were not added to the glue in the untreated specimen.

The intensities of nitrogen and boron are shown in Fig. 5 for plywood treated with 4% UMB. The distribution of nitrogen in the glue was similar to that of the untreated specimen; however, two boron peaks were distinct in the scan range where the nitrogen peaks diminished. The first boron peak appeared around the position of the assumed center of the glue, and the second peak was detected about 0.6 mm away from the first peak. It was believed that the boron migration occurred during the liquid or vapor phase of $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ in UMB-treated specimens while hot-pressing. Boron was assumed to migrate with the movement of the moisture under the heated conditions. When the heated moisture was not enough to transport the boron, it was thought to be left in the walls or lumens of the wood cells.

The intensities of nitrogen and phosphorus are shown in Fig. 6 for plywood treated with 4% UMP. The distribution of nitrogen is similar to that in Figs. 4 and 5. More obvious peaks were observed for phosphorus, which implied that

phosphorus distributed more uniformly near the interface between the veneer and the glue line. Compared with boron, phosphorus can easily move from the glue to wood during hot-pressing. Hence it is possible to provide these wood-based materials with more effective fire retardancy under certain conditions: that is, with glue additive treatment.

It is believed that leaching preservative chemicals from wood products causes a reduction of these effects and in their performance after long-term use. With the glue-additive method it is important that the chemicals can move from the glue and be transported into the wood cells. The optimized condition is possible by controlling the concentration of the chemicals, moisture amount, pressing condition, and so on. In this experimental condition, boron or phosphorus moved about 0.6 mm from the glue line, which greatly influenced the thickness of the overlay veneer that was incombustible.

SEM observations

The cross-sectional SEM micrographs of the interface between the core and the bottom layer of the untreated and the UMB- and UMP-treated plywoods after the incombustibility test are shown in Fig. 7. There was serious damage to

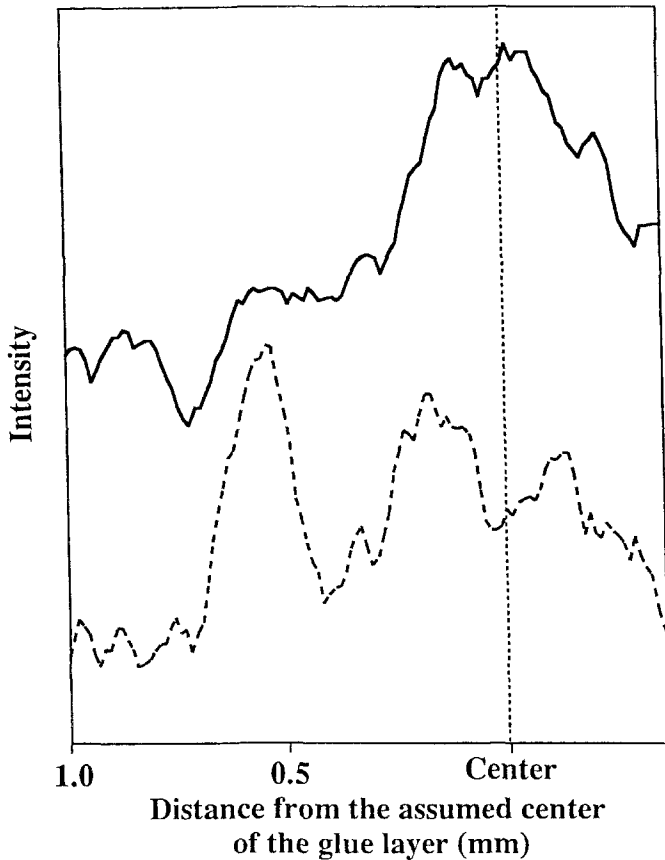


Fig. 6. Intensity of nitrogen and phosphorus in the 4% UMP-treated specimen. *Solid line*, nitrogen; *broken line*, phosphorus

the cell shapes and cell walls of the untreated specimen (Fig. 7A). The foamy structure along the interface between two veneer layers was thought to derive from the decomposition of urea melamine resin due to heat while testing with fire. When the wood was heated the cell walls lost their thickness owing to the decomposition of the walls and to the deformed cell arrangement and cell shapes.

Formed structures were not observed around the interface between the core and the bottom layer of the specimens treated with UMB, as shown in Fig. 7B. Some precipitates, which were present even after the fire test, were observed in cell lumens. The precipitates that appeared in the cell lumens were believed to be diboron trioxide, which is known to be able to prevent oxidation of carbon. It suggested that the UMB treatment effectively protected wood when the treated specimens were heated.

As shown in Fig. 7C, no blister was observed around the glue line in the specimen treated with UMP, although some precipitates were found in the cell lumens and along the knife checks. These precipitates were assumed to be composed of the resin and phosphate compound.

After exposure to fire, the cell structures retained their original shapes and arrangements, and the cell walls maintained their intact condition for both the UMP- and UMB-treated plywoods. Migration of boron or phosphorus from

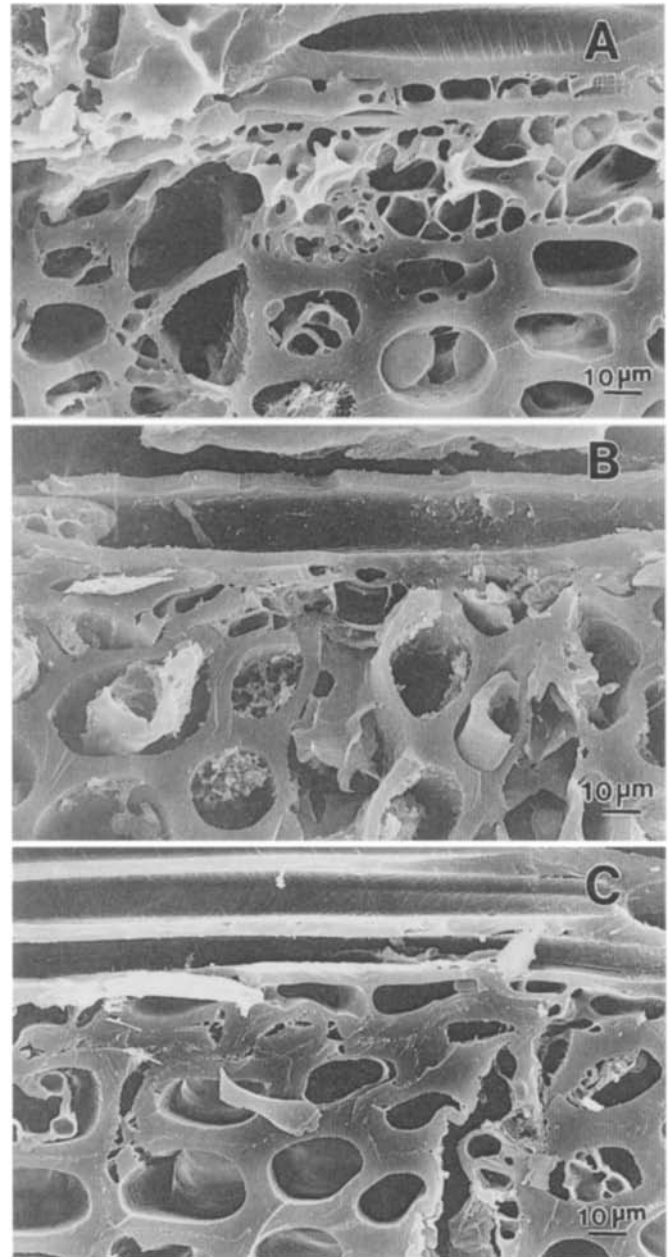


Fig. 7. Scanning electron micrographs of adhesive layers of plywoods after the flammability test. **A** Untreated. **B** Ammonium pentaborate addition. **C** Ammonium dihydrogen phosphate addition

the glue may contribute to the rest of the original wood structure after exposure to flames.

Effects of different thicknesses of overlaid veneers on incombustible properties

The influence of changing the thickness of the fire-exposed layer on the incombustibility of plywood was examined. When the added amount of the chemicals was adjusted at 2%, the glowing time was reduced for the specimens over-

laid with 0.6-mm surface layers after both UMP and UMB treatment; the difference was reduced at the higher chemical retention of 4%. Heat penetrated the glue line of specimens with the thinner overlaid layer more easily than those with the thicker surface layer. When the treating amount was 4%, the effectiveness of the fire-retardant chemical in the glue occurred within a shorter time for specimens with the thinner overlay than those with the thicker ones. On the other hand, the XPS line scan analysis showed that boron or phosphorus migrated from the glue line to the portion closed to the fire-exposed surfaces of the specimen, which improved the efficiency of glowing time reduction.

Better reduction of weight loss was observed from the specimens with the thicker surface overlay. Because the chemical elements migrated a greater distance close to the fire-exposed surface and distributed along the thickness for glue-additive plywoods, a large weight loss was observed only for the untreated specimens when exposed to flame. Although a similar trend was observed in the specimens with a thin or a thick overlaid surface, better performance was obtained for the specimens with the thick overlay veneer, which contained a larger amount of treated wood than the untreated plywoods.

The specimens overlaid with the thicker veneer displayed a reduced char length. It was demonstrated from the XPS line scan that the average migration distance of chemicals was almost the same as the thickness of the 0.6-mm overlaid veneer. It is believed that the thicker overlaid veneers retard carbonization and form a more stable char

layer on the surface than the thinner ones because the chemical elements distribute evenly along the thickness.

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References

1. Su Wen-Yu, Subyakto, Hata T, Imamura Y, Ishihara S (1997) Improvement of the fire retardancy of strandboard by surface treatment with melamine and boric or phosphoric acid. *Mokuzai Gakkaishi* 43:75–81
2. Su Wen-Yu, Yalinkilic MK, Hata T, Imamura Y, Ishihara S (1997) Enhancement of leach and termite resistances of plywood treated with boric compounds. *Mokuzai Gakkaishi* 43:595–601
3. Takahashi M, Tsunoda K, Imamura Y, Adachi A, Nishimoto K (1985) Studies on the production of preservative-treated plywood. I. Preservative effective of glue-line treated plywood with low toxicity chemicals. *Wood Preserv* 11:84–96
4. Subiyanto B, Yusuf S, Imamura Y, Fushiki S, Saito T, Katsuzawa Y (1994) Properties-enhanced albizzia particleboards by incorporating fungicide and insecticide in the glue. The 25th annual meeting of the International Research Group on Wood Preservation, Document No. IRG/WP/94-30060, Bali, May 29–June 3
5. Ogawa Y (1973) Flame-proof plywood (in Japanese). *Wood Ind* 28:241–245
6. Kodama T, Okada Y (1975) Possibility of new fire-retardant method for adhesive (in Japanese). *Ind Mater* 23:55–60
7. Imamura Y (1993) Estimation of the fungal resistance of wood composites for structural use. *Curr Jpn Mater Res* 11:75–84
8. JIS A 1322 (1966) Testing method for incombustibility of thin materials for building
9. Hilado CC (ed) (1973) Flame retardants, vol 6. Technomic Publishing, Westport, CT