

Photo-Deterioration of Chemically Modified Wood Surfaces: Acetylated wood and alkylated wood

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Abstract

Acetylation with acetic anhydride and alkylation with butylene oxide were applied to sugi (*Cryptomeria japonica* D. Don) veneers and blocks and the treated surfaces were evaluated for their photo-resistance using XPS (X-ray photo-electron spectroscopy) and colorimetry. Chemical modification treatments were expected to increase the weathering resistance of wood and the durability of weathering-resistant transparent type of coating films. Color changes on the chemically modified wood surfaces upon exposure to UV light were less conspicuous than those of untreated wood surfaces, but the photo-oxidation of modified wood surfaces, as estimated using XPS, was similar to that of untreated wood. Chemical modification did not increase the bonding strength or weathering resistance of transparent coating films.

Discipline: Forestry and forest products

Additional key words: weathering resistance, XPS, colorimetry, ultraviolet ray, transparent finishing

Introduction

The development of weathering-resistant woody materials which retain their natural color and appearance is a high priority in Japan and in many other countries. Since the weathering resistance of wood is poor, the development of new weather-proofing treatments is important. Finishing is one of the most effective treatments for increasing the weathering resistance of wood. Opaque coating films enable to avoid wood surface deterioration by light and to some extent water. Recently, highly durable clear finishes based on fluorine, acrylic or silicone resin, have been developed, which give more than 10 years service when applied to metals, ceramics or engineering plastics. Such finishes persist for a long time because the films do not absorb UV and the underlying substrates are also resistant to UV. However, the durability of such coatings on wood lasts only 2 to 3 years because of the low resistance of wood to UV light. Therefore it is necessary to develop effective methods of photo-stabilization of wood surfaces if the durability of such finishes on wood is to be increased (Fig. 1).

Aromatic compounds on the wood surface, such

as lignin or organic solvent-soluble extractives, absorb UV and are degraded by photo-oxidation³⁾. Studies on the discoloration of thermo-mechanical pulp (TMP) have shown that phenolic hydroxyl groups are the sites for the radical reactions involved in photo-oxidation⁶⁾. In general, the dimensional stability and decay resistance of wood are improved

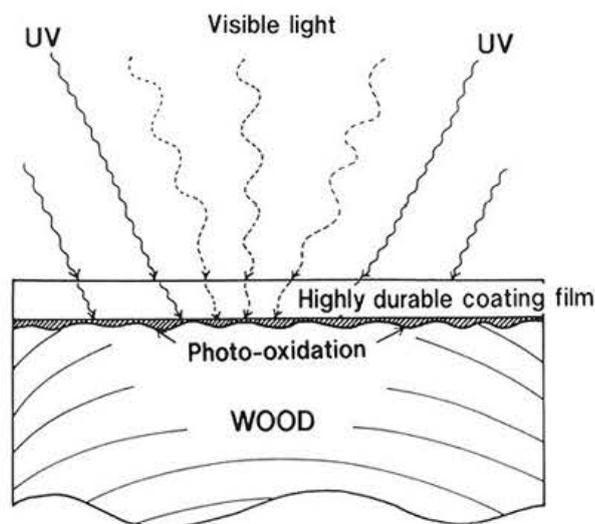


Fig. 1. Photo-oxidation of wood surface under transparent coating films

by substitution of hydroxyl groups in wood with hydrophobic functional groups⁹⁾. However, it remains to be determined whether such a substitution increases the weathering resistance of wood and there have been few studies on the weathering resistance of chemically modified wood in spite of the increasing importance of chemical modification treatments. In this study, the photo-resistance of chemically modified wood was evaluated after UV irradiation, using colorimetry and XPS. The bonding strength and durability of a clear finish on modified wood surfaces were also evaluated. The aim was simply to determine whether chemical modification by acetylation and alkylation increased the UV resistance of wood and the durability of a clear coating during outdoor exposure.

Materials and methods

1) Materials

Sugi (*Cryptomeria japonica* D. Don: Japanese cedar) heart-sliced (quartersawn) veneers, 0.2 mm in thickness, and blocks, 35 × 25 × 7 mm (longitudinal × radial × tangential dimensions), were used in this study. The specific gravity of the blocks on an oven-dried basis ranged from 0.28 to 0.35. Specimens were extracted with a mixture of ethanol and benzene (1:2 v/v) for 24 h and then vacuum-dried for 48 h at 60°C.

2) Chemical modification of wood surfaces

(1) Acetylation

Oven-dried specimens of sugi veneers and blocks were acetylated using liquid or vapor phase reactions.

Table 1. Illumination supplied by 20 W UV fluorescent lamps

Sensor	UV-25	UV-31	UV-35	UV-42
Sensitivity (nm)	241–320	290–350	320–390	330–490
Peak wave length (nm)	254	310	350	420
20 W UV fluorescent lamp (distance of 15 cm) (mW/cm ²)	0.013	0.136	1.100	0.456
400 W High pressure mercury lamp (distance of 15 cm) (mW/cm ²)	1.350	2.790	3.490	7.220
Solar radiation (August 7, at noon) (mW/cm ²)	0.942	2.280	2.410	11.000

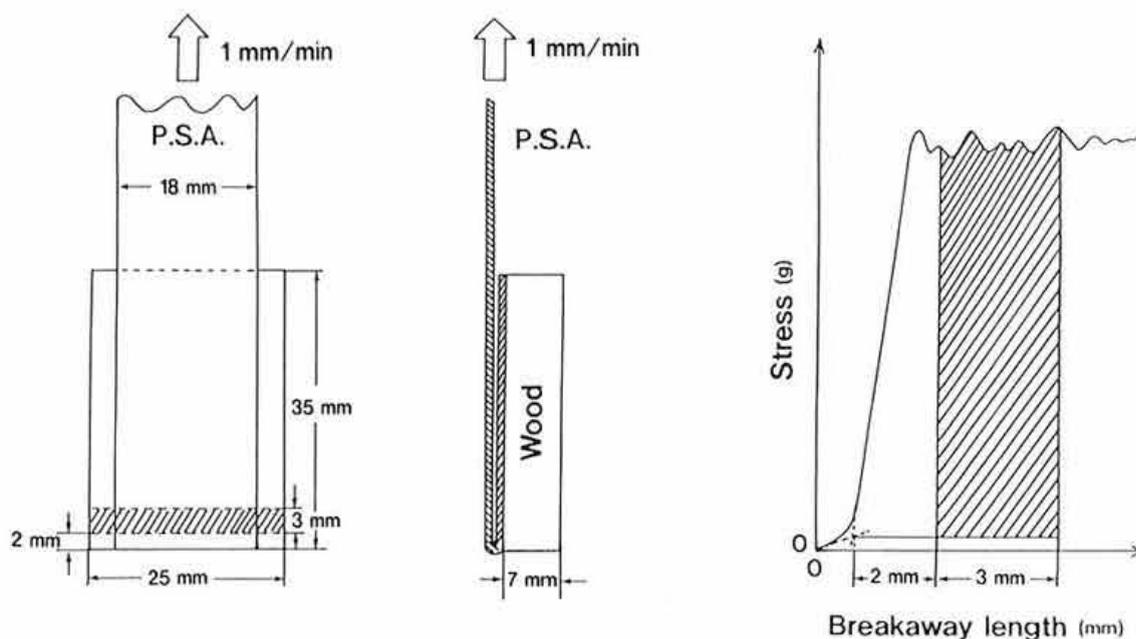


Fig. 2. Peeling test for measurement of bonding strength on the wood surface
P.S.A.: Pressure-sensitive adhesives.

In the case of liquid phase acetylation, specimens were soaked in a mixture of acetic anhydride and xylene (1:1 v/v) and reacted at 120°C for 8 h under about 1 Mpa pressurized nitrogen gas⁸⁾. For the vapor phase acetylation, blocks were put in a reaction chamber with acetic anhydride, and the chamber was heated at 150°C for 12 h. Reacted specimens were washed in running water and dried. Averaged weight percent gains (WPGs) of veneers and blocks after liquid phase acetylation were about 20.5 and 18%, respectively. WPGs of veneers acetylated in the vapor phase averaged about 16.6%.

(2) Alkylation with butylene oxide

Alkylation was also undertaken in the liquid and vapor phases. For the former, oven-dried veneers and blocks were soaked in a mixture of butylene oxide and triethylamine (95:5 v/v), and reacted for 8 h at 120°C under pressured nitrogen¹⁰⁾. For the vapor phase alkylation, veneers were put in a reaction vessel with a mixture of butylene oxide and triethylamine (95:5 v/v), and the vessel was heated at 120°C for 12 h. Specimens were then washed with water and dried. Average WPGs of veneers and blocks after liquid phase alkylation were about 23.7 and 25.3%, respectively. WPGs of veneers alkylated in the vapor phase averaged about 32.0%.

(3) UV ray irradiation test

Treated specimens were irradiated with UV using four 20 W UV fluorescent lamps in an air-conditioned chamber at 25°C and 65% relative humidity (RH). The distance from the lamps to the specimens was 150 mm, and the maximum irradiation time was 500 h. The intensity of the UV light on the surface of the samples is shown in Table 1. Untreated sugi wood meals were also irradiated with UV, and the amount of alkali (1% NaOH)-soluble extractives was measured after irradiation.

(4) XPS analysis

After irradiation, specimens 0.5 mm thick were cut from blocks. These specimens and veneers were analyzed using XPS (Shimadzu ESCA 850). A soft X-ray source (Mg: magnesium) was generated using a power source of 8 kV and 30 mA. The vacuum conditions were $5 \times 10^{-6} \sim 1 \times 10^{-5}$ Pa. The C(1s) and O(1s) spectra were measured. Curve fitting of the spectra was calculated using the Gaussian formula. Photo-oxidation of wood surfaces was evaluated by examining the increase in the carbonyl and carboxyl area of the C(1s) spectrum and the ratio of oxygen versus carbon (O/C).

(5) Bonding strength

For the measurement of the photo-deterioration

of wood surfaces, the peeling strength between specimens surfaces and pressure-sensitive tape was measured. The working ratio was then calculated (Fig. 2).
(6) Colorimetric analysis

Color change of the wood surfaces after UV irradiation was determined using a colorimeter (Minolta CR-200). Color change (ΔE^*) was calculated using L*, a*, b* colorimetric system.

(7) Finishing and outdoor exposure test of chemically modified wood

Specimens chemically modified by vapor phase were finished with a transparent acrylic silicon

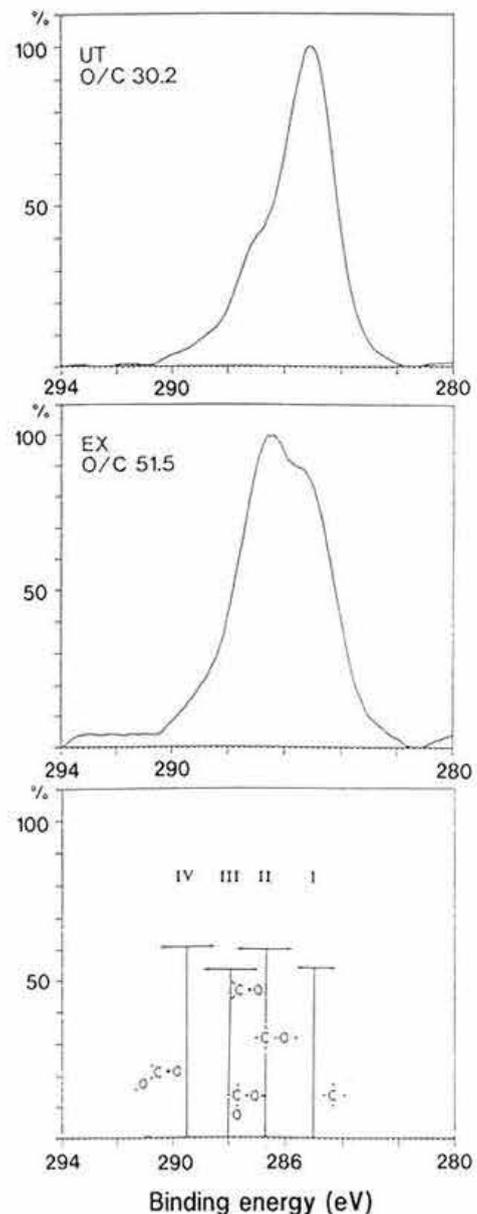


Fig. 3. XPS C(1s) spectra of sugi-veneer surfaces
UT: Untreated sugi, EX: Sugi extracted with ethanol-benzene.

varnish produced by Kyushu Toryo Co. Ltd. These specimens were exposed to the south in the weathering test field of FFPRI in Tsukuba city.

Results and discussion

1) Photo-deterioration of untreated wood surfaces

The XPS C(1s) spectra of untreated and ethanol-benzene extracted sugi veneer surfaces are shown in Fig. 3. The binding energy of C(1s) spectrum of organic materials was first examined by Dorris and Gray¹⁾. The C(1s) spectrum of untreated sugi surface shows that the surfaces are hydrophobic because the main binding energy of the peak at around 285 eV is characteristic of hydro-carbon bonding such as C-C or C-H. In general, timbers or veneers are subjected to cutting and drying processes before they are used, and during such processing water in wood migrates centrifugally, depositing hydrophobic fatty acids and resins on the wood surface¹¹⁾. However, after extraction with an ethanol and benzene mixture, these extractives are removed and the surface shows hydrophilic properties. Thus the XPS spectrum of such surfaces shows a large increase in carbon-to-oxygen bonding at around 287 eV.

Fig. 4 illustrates XPS C(1s) spectra of sugi surfaces after irradiation with fluorescent UV. The

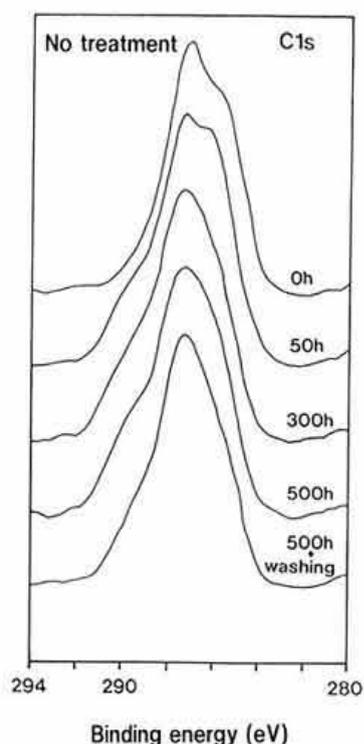


Fig. 4. XPS C(1s) spectra of sugi surfaces after irradiation with fluorescent UV

area of the peak at above 288 eV, which was characteristic of carbonyl and carboxyl groups, increased and that at around 285 eV decreased. This phenomenon may be ascribed to the degradation by UV of aromatic compounds on the wood surface such as lignin or extractives, resulting in the formation of carbonyl or carboxyl groups³⁾. The XPS C(1s) spectrum of the irradiated surface after aqueous leaching indicated that the carbonyl or carboxyl area had decreased, presumably because photo-oxidized materials and decomposed aromatic compounds on the wood surface were water-soluble and were washed away by water. The irradiated and leached surfaces were rich in cellulose because the main peak was associated with C-O bonding at around 287 eV.

Fig. 5 shows the relationships between the irradiation time and the amount of alkali-soluble extractives and O/C ratio of XPS of untreated sugi veneer surfaces. The extractive content and the O/C ratio rapidly increased during the initial stages of irradiation, but thereafter remained relatively constant. It appears that pronounced photo-oxidation of aromatic compounds on the wood surface occurred during the initial stages of UV irradiation and thereafter, the reaction sites on the surfaces decreased and perhaps more oxidized carbon was released as CO₂ gas⁴⁾. The amount of extractives exceeded 20% and the O/C ratio was about 70% after irradiation with UV light for 500 h. It is likely that when such photo-deterioration of wood surfaces occurs under UV-transparent coating films, the bonding strength of the coating films on the wood surface may decrease.

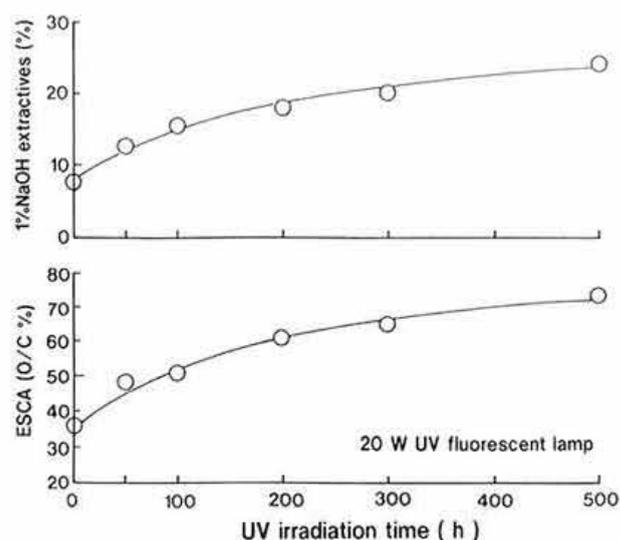


Fig. 5. Relationship between irradiation and the amount of alkali-soluble extractives and O/C ratio of XPS of untreated sugi veneer surfaces

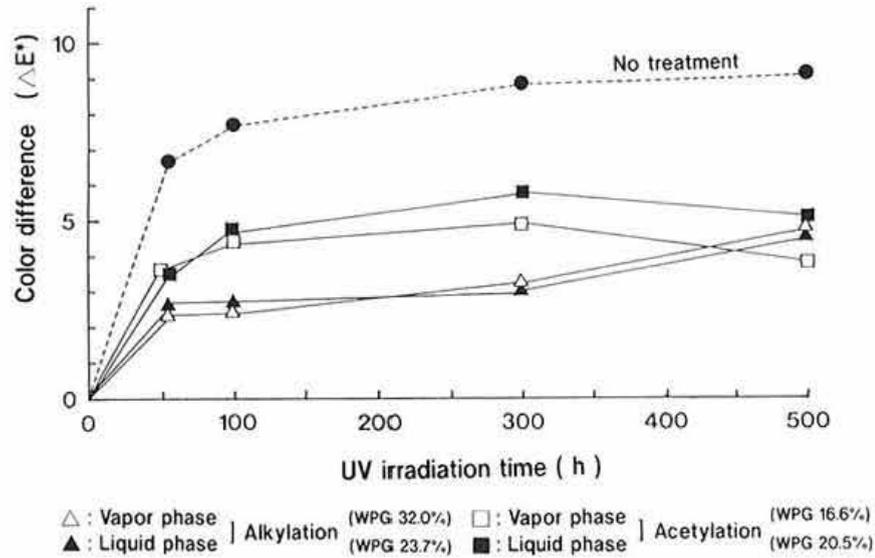


Fig. 6. Color difference (ΔE^*) of chemically modified wood after UV irradiation

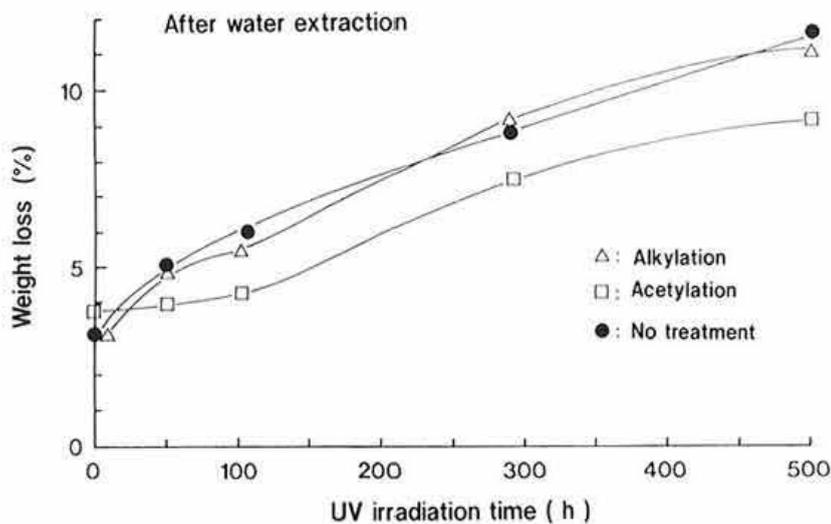


Fig. 7. Relationship between weight percent loss of chemically modified wood meals due to irradiation and water extraction

Films would then be very easily detached from the degraded wood surfaces.

2) Photo-deterioration of chemically modified wood
 (1) Color difference

Fig. 6 shows the color difference (ΔE^*) of chemically modified wood after UV irradiation. The color difference of acetylated and alkylated woods was less significant than that of untreated surfaces. Phenolic hydroxyl groups of wood were probably substituted by acetyl or butyl groups during chemical modifications, and these groups prevented the formation of radicals by UV irradiation, and reduced the forma-

tion of colored quinone structures. For all the specimens, the color difference (ΔE^*) mostly increased until 100 h and then became almost constant. In the initial stage, the value of the color difference of alkylated wood was lower than that of acetylated wood.

(2) Weight loss

Fig. 7 shows the relationships between the weight percent loss of chemically modified wood meals as a result of irradiation and water extraction. Weight percent loss (WPL) of all the samples increased with increasing irradiation time. WPL of alkylated wood was almost the same as for untreated wood, while

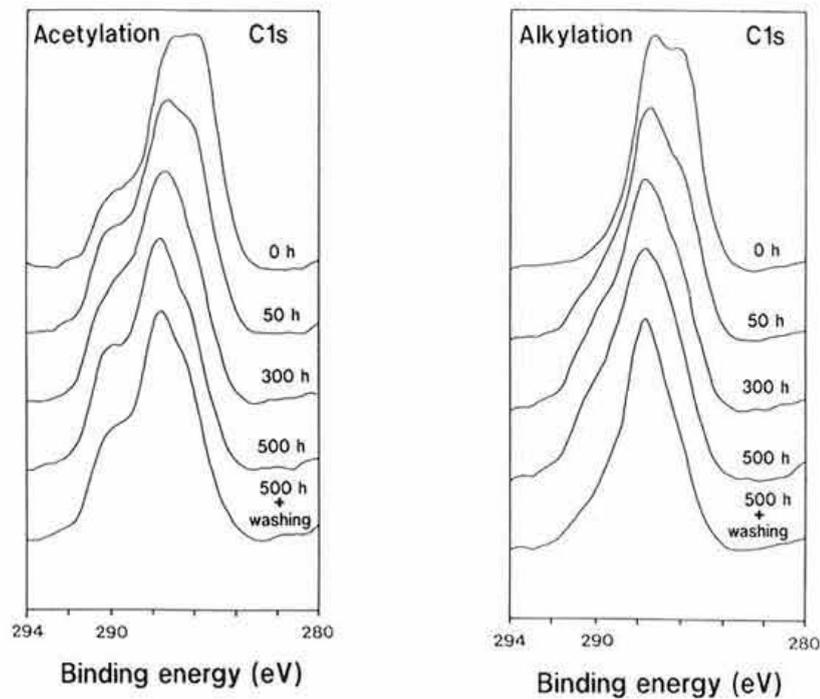


Fig. 8. XPS C(1s) spectra of acetylated and alkylated wood surfaces after UV irradiation

that of acetylated wood was lower. Fig. 8 shows the XPS C (1s) spectra of acetylated and alkylated wood surfaces after UV irradiation. The aromatic compounds of acetylated and alkylated wood surfaces decreased and the oxidized region of the XPS spectrum expanded with increasing UV irradiation. Kalnins reported that acetylated wood was more sensitive to photo-oxidation than untreated wood^{4,5}. Evans reported²) that acetylation reduced the initial losses of lignin degradation products from wood during outdoor exposure because the wood surfaces were more hydrophobic. However, the photo-protective effects of acetylation on lignin were lost with prolonged exposure of wood to weathering. He also suggested that the substitution of hydroxyl groups which prevents the formation of quinone structures with UV-absorbing properties may not exert beneficial effects on the weathering of wood²). For alkylation, it is considered that the reactivity of the epoxy radical to hydroxyl groups of wood is higher, and that the amorphous region of wood is modified by butylene oxide and triethylamine solution¹⁰). These facts indicate that both chemical treatments were ineffective in protecting the wood surfaces against photo-deterioration.

(3) Natural weathering of chemically modified wood

Fig. 9 shows the XPS spectra of untreated and chemically modified wood surfaces after outdoor

exposure for 10 months. Although the height of the C-O peak in untreated wood increased with the increase of the duration of the exposure period, the height of the carbonyl or carboxyl peak did not increase after outdoor exposure possibly because water-soluble photo-degradation products were leached from the wood surface by rain. For acetylated wood, the height of the peaks of C-O and oxidized carbon increased during outdoor exposure to a similar extent to that of untreated wood. Acetyl groups on the acetylated wood surface were also photo-decomposed and washed away. The XPS spectra of alkylated wood after weathering were similar to that of untreated wood. Although Plackett reported that acetylated wood showed a high weathering resistance⁷), the results here suggest that chemical modification does not significantly improve the weathering resistance of wood.

(4) Bonding strength

Fig. 10 shows the bonding strength of the tape on chemically modified wood surfaces. Bonding strength was lower on alkylated wood than on untreated or acetylated wood. Rowell reported that alkylation with butylene oxide swelled wood beyond its green volume because of polymerization of butylene oxide¹⁰), resulting in damage to the cell wall structures. Fig. 11 shows the percentage losses in the bonding strength of the tape on chemically

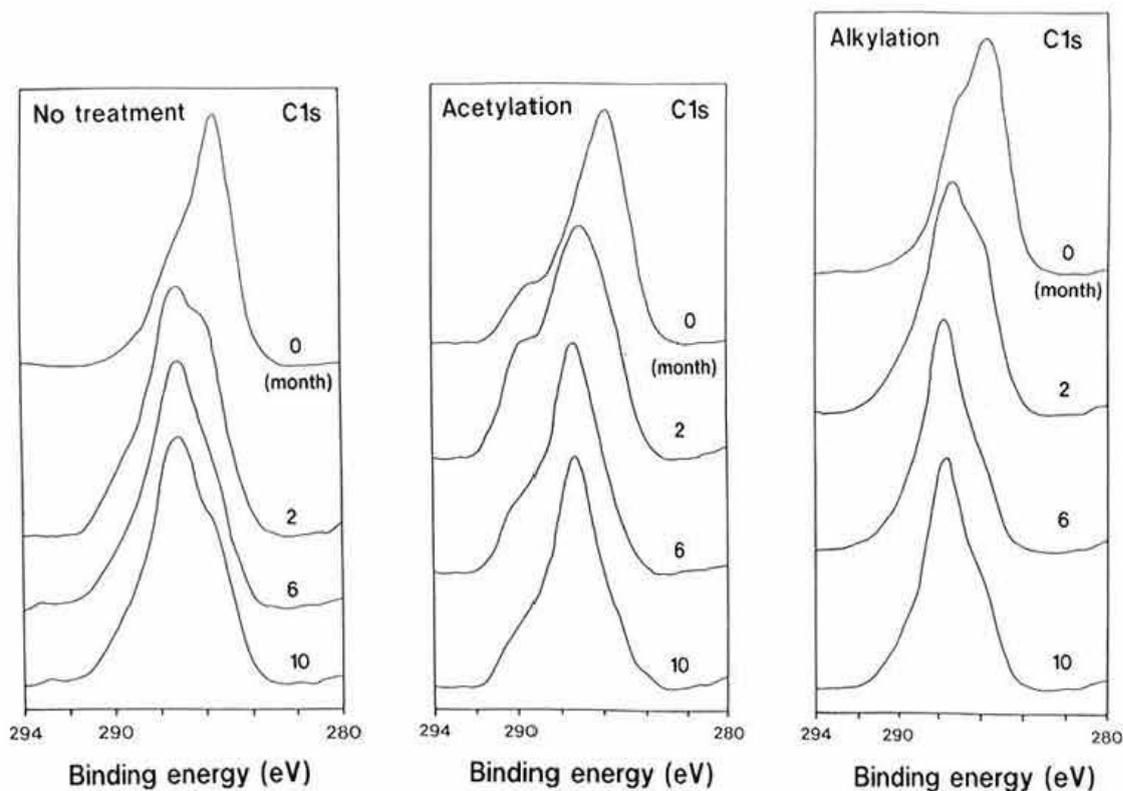


Fig. 9. XPS C(1s) spectra of untreated and chemically modified wood surfaces after outdoor exposure for 10 months

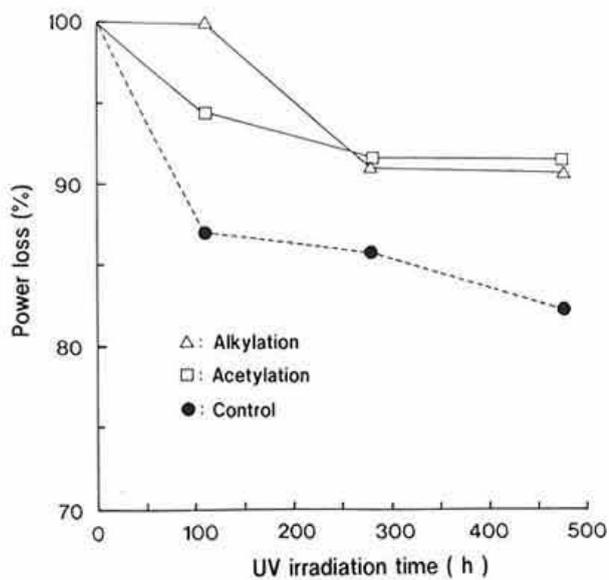


Fig. 10. Bonding strength of the tape on chemically modified wood surfaces during UV irradiation

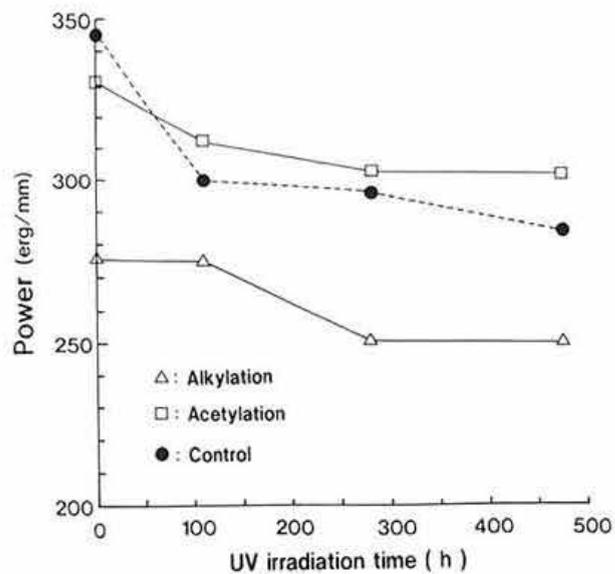


Fig. 11. Bonding strength percent loss of the tape on chemically modified wood surfaces during UV irradiation

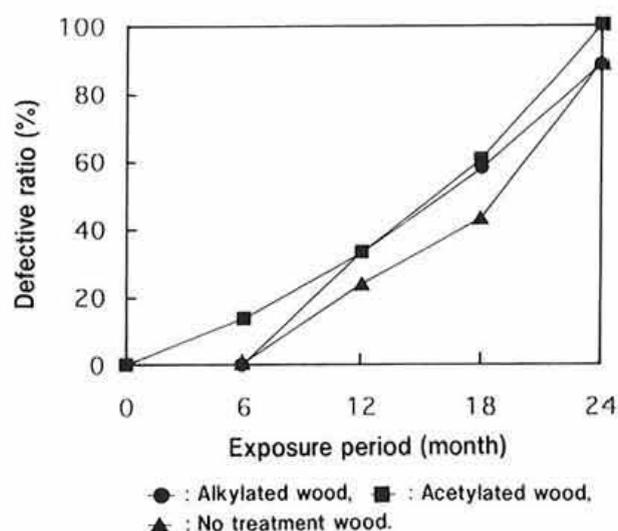


Fig. 12. Deterioration of a transparent type of acrylic silicon varnish on chemically modified wood during an outdoor exposure

modified wood surfaces during UV irradiation. Initial losses on untreated wood were bigger than those on chemically modified woods. Deterioration of a transparent type of acrylic silicon varnish on chemically modified wood during an outdoor exposure test for 2 years is shown in Fig. 12. The durability of the films was lowest on acetylated wood, and was slightly lower on alkylated wood than on untreated wood. It is suggested that the durability of the coating was affected not only by photo-oxidation of the wood surface but also by the polarity, acidity and/or mechanical strength of the wood surface.

Conclusion

Photo-deterioration of wood surfaces chemically modified by acetylation and alkylation was studied. The color change of the chemically modified wood surfaces was less pronounced than that of untreated wood because of the substitution of phenolic hydroxyl groups by the chemical modification, which prevents the formation of quinones. XPS analysis, however, indicated that chemical modification did not prevent the photo-oxidation of wood surfaces and such surfaces were degraded to the same extent as untreated

wood. Bonding strength of wood surfaces was evaluated by a peeling test using pressure-sensitive tape. The bonding strength of tape on the chemically modified wood was lower than on untreated wood and there were no significant differences in the durability of a transparent finishing coating on the chemically modified wood compared to that on untreated wood.

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