

Protection of Wood Surfaces against Photooxidation

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Synopsis

Protection of wood surfaces against photoinduced oxidative degradation can be achieved by using effective coating agents. Several penetrating chemical agents, such as triol-G 400, PEG-G 400, and 1-octadecanol, were shown to provide good protection for wood surfaces against discoloration during ultraviolet irradiation. In addition, wood surfaces coated with clear film-forming finishes, such as homo- and copolymers of 2-hydroxy-4 (3-methacryloxy-2-hydroxypropoxy) benzophenone, exhibited outstanding performance into inhibiting discoloration and surface deterioration. Infrared and ultraviolet absorption spectra and scanning electron microscopy studies revealed that the clear polymeric coatings containing an internal UV absorber were very stable and resistant to photooxidation. Possible chemistry and mechanisms of protection of wood surfaces provided by these polymeric coating systems are discussed.

INTRODUCTION

Wood in its outdoor applications must satisfy a number of criteria, and, of these, stability to prolonged sunlight exposure is one of the most important. In the natural outdoor environment, wood without a protective coating or treatment, undergoes discoloration, loss of brightness, i.e., lightness, surface roughening, and checking when exposed to terrestrial sunlight in the presence of oxygen.¹ At the microscopic level, the chemical nature of the wood surface is changed, and the ultrastructure of wood cell walls is damaged.^{2,3} Although this weathering process develops primarily at the surface of wood, the susceptibility to photooxidative degradation significantly reduces wood's aesthetic values and performance. Meanwhile, due to the current shortage in the supply of good quality wood, attempts to improve wood appearance and performance against photooxidation have aroused interest in the forest products and coatings industries.

A great deal of effort has been put into the development of protective systems for wood to prevent photodegradation during outdoor weathering. Numerous inorganic treatments have been investigated and shown to impart beneficial properties to wood for outdoor applications.⁴⁻⁷ Recent research²⁻⁴ has shown that the photodegradative effect on wood surfaces can be mitigated by treating them with aqueous solution of ferric chloride and chromium trioxide. However, most of the inorganic treatments stained the wood strongly, giving an unattractive appearance. On the other hand,

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a wide variety of organic finishes such as paints and solid color stains have been applied to wood-based products⁸⁻¹³ to achieve a good degree of protection against photodegradation. Unfortunately, these finishes conceal the aesthetic wood grain and, to some extent, characteristic texture of wood. The use of clear coatings to retain the natural appearance and color of wood would be very beneficial. However, the performance of transparent coatings against photooxidative degradation is regrettably poor since most of the available clear finishes are sensitive to ultraviolet light and readily lose their protective function. In addition, ultraviolet light can penetrate through them to initiate photochemical reactions at underlying wood surfaces resulting in discoloration and cohesion failure between wood and coating system.

In view of this need for stable, transparent coatings for wood, a clear acrylic coating containing an internal ultraviolet light absorber, 2,4-dihydroxybenzophenone (2,4-DHBP), was developed and its protective functions against photooxidative degradation was evaluated. Its effectiveness was compared to several penetrating chemical agents. In some cases, additional antioxidants were added to the coatings to repress oxidation reactions and to enhance the protective effect.

TABLE I
Commercially Available Ultraviolet Stabilizers

Trade Name	Producer	Chemical structure
Tinuvin 770	Ciba-Geigy Ltd.	
Irganox 1010	Ciba-Geigy Ltd.	
BHT ^a	Hercules	
DABCO ^b	Eastman Kodak	
Mark-1409 ^c	Witco Chem. Co.	

^a 2,6-Di-*tert*-butyl-4-methylphenol.

^b 1,4-Diazabicyclo(2,2,2)octane or triethylenediamine (TEDA).

^c Phosphite chelator.

EXPERIMENTAL

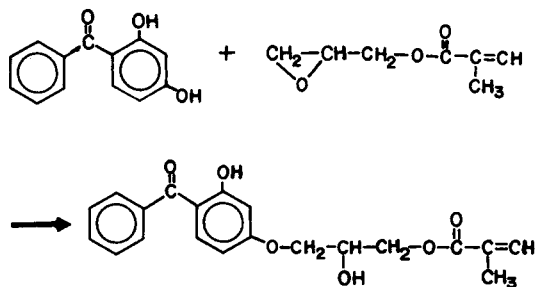
Materials

Wood Materials. Southern yellow pine (*Pinus* spp.) was selected for this study. Wood blocks with dimensions of $0.75 \times 0.75 \times 1$ in. were softened by soaking them in distilled water prior to microtoming. Tangential microtomed sections of earlywood with $25 \mu\text{m}$ thickness were prepared for the examination of chemical changes. Specimens with microtomed transverse surfaces were prepared for microstructural study using a scanning electron microscope. Wood panels with dimensions of $2 \times 2 \times 0.75$ in. were prepared for the brightness and color measurements. All specimens were air-dried at ambient temperature prior to any ultraviolet irradiation.

Coating Agents. Two types of treatments systems were prepared for this study. The first, penetrating chemical agents, included triol-G 400 (Jefferson Chemical Co.), poly(ethylene glycol) (PEG-400; Olin Mathieson Chemical Co.), and 1-octadecanol (Eastman Kodak Co.). The second, film-forming finishes, included cellulose nitrate, polyurethane, linseed-tung phenolic varnish, poly[2-hydroxy-4(3-methacryloxy-2-hydroxy-propoxy) benzophenone] [poly(HMHBP)] and its copolymer with alkyl acrylate. The first three film-forming finishes were commercially available products. Poly(HMHBP) was synthesized in the laboratory according to Fertig and his co-workers.¹⁴ Details are described in a subsequent section. The copolymer of HMHBP was obtained from National Starch and Chemical Corp. Five commercially available ultraviolet light stabilizers were also used in these studies (Table I).

Procedure

Preparation of 2-Hydroxy-4(3-Methacryloxy-2-Hydroxy-Propoxy) Benzophenone (HMHBP). The ultraviolet absorbing monomer, HMHBP, was synthesized according to the following reaction¹⁴:



Scheme 1

Under a nitrogen atmosphere, 1 mol (214 g) of 2,4-DHBP and 1.1 mol (156 g) of glycidyl methacrylate was heated with stirring at $78 \pm 2^\circ\text{C}$ for 5 h in the presence of 3 g ammonium nitrate in 500 mL benzene. After neutralizing the reaction solution with 1% sulfuric acid and drying over magnesium sulfate for 20 h, the benzene was removed under reduced pressure, obtaining a 95% yield of monomer (HMHBP). The chemical structure of HMHBP was characterized by IR and ultraviolet spectroscopy (Figs. 1 and 2).

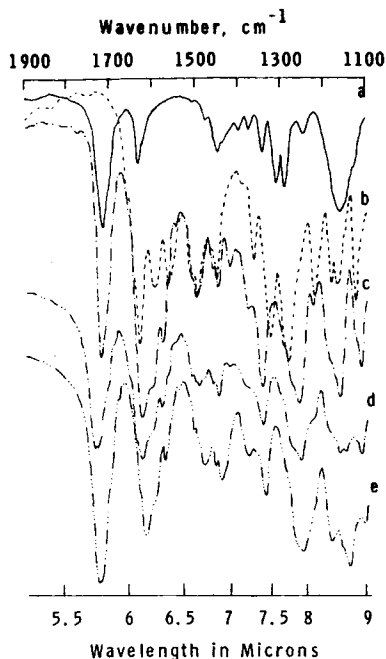


Fig. 1. Infrared spectra of ultraviolet-stabilizing monomer, polymers, and its starting materials: (a) glycidyl methacrylate; (b) 2,4-dihydroxybenzophenone; (c) HMHBP; (d) poly(HMHBP); (e) copoly(HMHBP).

Preparation of Poly[2-Hydroxy-4(3-Methacryloxy-2-Hydroxy-Proxy) Benzophenone] [Poly(HMHBP)]. The homopolymer, poly(HMHBP), was prepared by polymerization of 330 g HMHBP monomer in 70 g tetrahydrofuran (THF) in the presence of 0.15 g azobisisobutyronitrile (AIBN) as initiator, at 70°C for 6 h. The polymeric product was isolated by precipitation from methanol. The polymer was a light yellow powder soluble in acetone, THF, and dioxane, but insoluble in methanol, benzene, and

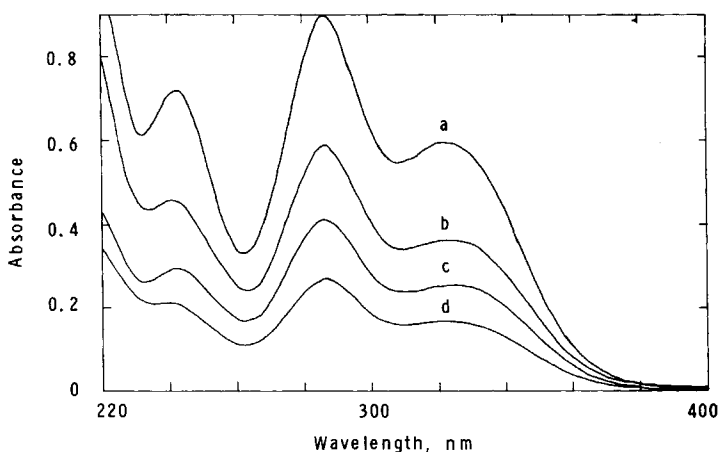


Fig. 2. UV absorption spectra of: (a) 2,4-dihydroxybenzophenone; (b) HMHBP; (c) poly(HMHBP); (d) copoly(HMHBP).

acetate. The chemical structure of poly HMHBP was characterized by IR and ultraviolet spectroscopy (Figs. 1 and 2).

Preparation of Coating Systems. Surface treatments used in this study are summarized in Table II.

Ultraviolet Light Irradiation. A high-pressure quartz mercury xenon compact arc lamp (Conrad-Hanovia, lamp type 901 B0011, 200W) with wavelengths longer than 254 nm, and a high-pressure quartz mercury vapor lamp (ACE-Hanovia, lamp type 6531-12, 200W) with wavelengths longer than 220 nm were used. Specimens for brightness and color measurements (using a brightness tester and colorimeter manufactured by Technidyne Corporation; Model S-4) and for the scanning electron microscopic study (using SEM Model 900; Advanced Metal Research Corp.), were mounted on a test shelf and exposed to ultraviolet light directly at a distance of 50 cm. For the study of chemical changes on protected wood surfaces, microtomed tangential earlywood sections were mounted behind a coating film and then exposed to ultraviolet light. The surface was analyzed using an infrared spectrophotometer (Beckman Model Acculab-8). A Cary-219 ultraviolet-visible spectrophotometer (Varian Associates) was used to study the degradation products. The molecular weight of poly(HMHBP) was determined using a Knauer Vapor Pressure Osmeter equipped with a universal thermistor probe. The calibration curve was prepared based on 2,4-DHBP. Dimethylformamide (DMF) was used as a solvent. The thermal behavior of the irradiated and nonirradiated specimens was studied with a Perkin-Elmer differential scanning calorimeter (DSC), Model DSC-4, equipped with a system for microcomputer controller which offers the memory facilities for long-term storage of complete analytical routines.

TABLE II
Summary of the Wood Surface Treatments

No.	Ingredients	Solvent	Solid content (%)
1	PEG-400	Water	20
2	PEG-400	Chloroform	10
3	Triol-G400	Water	20
4	1-Octadecanol	Chloroform	10
5	PEG-400 + 1-octadecanol (2:1 w/w)	Chloroform	30
6	PEG-400 + 1-octadecanol (1:1 w/w)	Chloroform	20
7	PEG-400 + 1-octadecanol (2:1 w/w)	Chloroform	15
8	Nitrocellulose	Acetone	10
9	Polyurethane	Mineral spirits	10
10	Linseed-tung phenolic resin	Mineral spirits	10
11	Poly(HMHBP)	Acetone	10
12	Copoly(HMHBP)	Acetone	10
13	Copoly(HMHBP) + tinuvin-770 (9:1 w/w)	Acetone	10
14	Copoly(HMHBP) + irganox-1010 (9:1 w/w)	Acetone	10
15	Copoly(HMHBP) + BHT (9:1 w/w)	Acetone	10
16	Copoly(HMHBP) + DABCO (9:1 w/w)	Acetone	10
17	Copoly(HMHBP) + Mark-1409 (9:1 w/w)	Acetone	10
18	PEG-400 + poly(HMHBP)	Water/acetone	20/10
19	PEG-400 + 78-6121	Water/acetone	20/10
20	Triol-G400 + poly(HMHBP)	Water/acetone	20/10
21	Triol-G400 + 78-6121	Water/acetone	20/10

RESULTS AND DISCUSSION

Characterization of HMHBP and Poly(HMHBP)

A 95% yield of monomer, HMHBP, was obtained as a viscous yellow liquid by the reaction of 2,4-DHBP with glycidyl methacrylate, using ammonium nitrate as a catalyst. HMHBP was successfully polymerized in solution in THF with AIBN as initiator to give homopolymer, poly(HMHBP). The homopolymer was obtained in about 70% yield after 6 h at 70°C. The copolymer obtained from National Starch and Chemical Corp. was prepared by copolymerization of HMHBP with an alkyl methacrylate (1:1 w/w).

The infrared spectra of homopoly(HMHBP) and copoly(HMHBP) compared to the starting materials are shown in Figure 1. They all showed the 1725 cm^{-1} absorption band due to the carbonyl stretching vibration of glycidyl methacrylate and the band at 1630 cm^{-1} due to the carbonyl stretching vibration of 2,4-DHBP. The characteristic broad absorption band due to —OH stretching vibration was observed near the 3400 cm^{-1} region.

The ultraviolet spectra of 2,4-DHBP, HMHBP, and poly(HMHBP) are similar (Fig. 2). They all exhibited three absorptions, namely, at 242, 286, and 324 nm, the characteristic absorption of 2,4-DHBP.

The number average molecular weight of homopoly(HMHBP) determined by a Knauer vapor pressure osmometer, was 10,800 (Table III). That of copoly(HMHBP) provided by National Starch and Chemical Corp. was about 10,000. The thermal behavior of homopoly(HMHBP) was examined using a differential scanning calorimeter (DSC). Homopoly(HMHBP) exhibited a glass transition temperature at 78°C (Fig. 3). Other properties of the polymer and its copolymer with alkyl methacrylate are summarized in Table III.

Discoloration of Wood Surfaces

Color, because of its aesthetic value, is very important in the utilization of wood for decorative applications. Wood color is a composite property whose value is relative to its basic chemical composition. Because of its color, wood is sensitive to light.¹⁵ The photochemistry of wood always involves chemical as well as physical changes.

TABLE III
Properties of Homopolymer and Copolymer

	Homopoly(HMHBP)	Copoly(HMHBP)
Molecular weight	10,830	10,000
T_g (°C)	78	
Soluble	Acetone, THF, and dioxane	Acetone, ethyl acetone, methyl cellulose, methyl ethyl ketone, methylene chloride, dimethylfuran, and dimethyl acetamide
Insoluble	Water, methanol, benzene, and ethyl acetate	Water, methanol, and ethanol

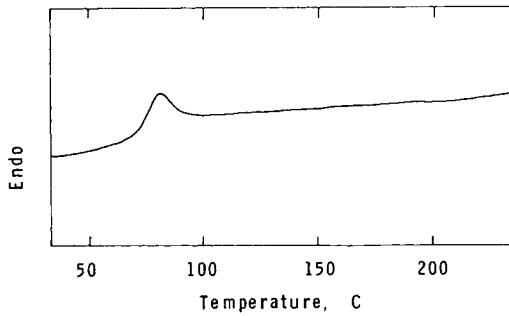


Fig. 3. DSC thermogram of homopoly(HMHBP).

When unprotected southern pine wood was exposed to ultraviolet light, the immediate visible change of the surface properties was discoloration. Nonirradiated wood was initially light yellow, but, after exposure to ultraviolet light of $\lambda > 254$ nm, the original color of the wood surface changed from yellow to light brown and dark brown. The changes in brightness and color of wood surfaces are illustrated in Figure 4. During the first few days of exposure, the decrease in brightness (i.e., lightness) and the change in color was significant. After 40 days of exposure, the brightness retention dropped down to 42% and a color change of ΔE_{ab} of 14 in the CIE-LAB color space. These results show that ultraviolet light causes rapid and significant changes in the brightness and color of exposed wood surfaces.

Wood Surfaces Treated with Penetrating Finishes

The protective effect against ultraviolet irradiation provided by penetrating finishes, which leave little or no continuous coating on the wood surface, was monitored by measuring changes in brightness (i.e., lightness) and color after irradiation.

Selected chemical solutions, when applied to wood surfaces, provided a degree of protection against ultraviolet degradation as seen in the changes in brightness and color (Figs. 5 and 6). After 40 days irradiation, the brightness retention of untreated wood was 43% whereas the wood treated with

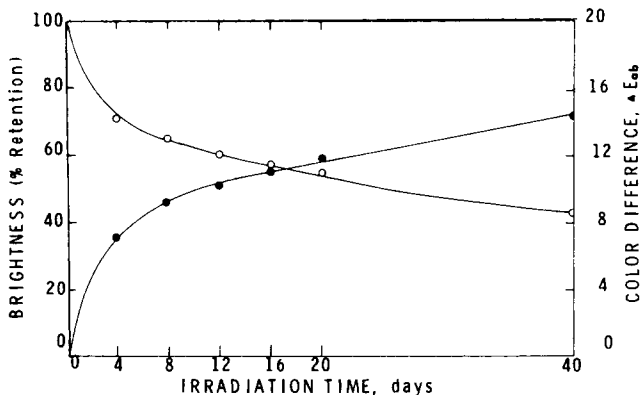


Fig. 4. Changes in brightness (○) and color (●) of southern yellow pine exposed to ultraviolet light ($\lambda > 254$ nm).

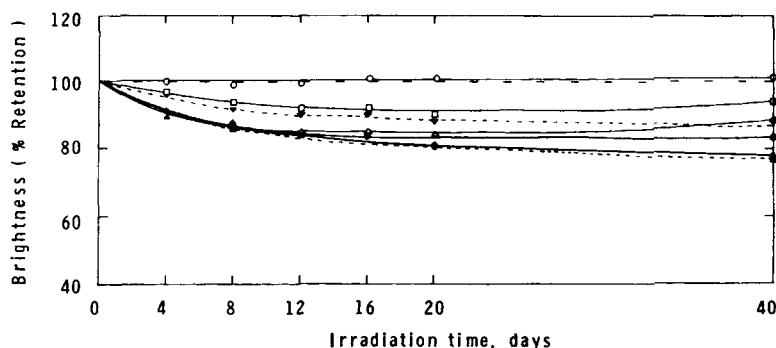


Fig. 5. Change in brightness of irradiated southern yellow pine treated with penetrating finishes: (Δ) 20% triol-G400; (\blacktriangle) 20% PEG-400; (\blacksquare) 10% PEG-400; (\bullet) 10% 1-octadecanol; (\square) 10% PEG-400 + 10% 1-octadecanol; (\circ) 20% PEG-400 + 10% 1-octadecanol; (\blacktriangledown) 10% PEG-400 + 5% 1-octadecanol.

penetrating finishes showed higher brightness retention. Although wood treated with 20% PEG-400 solution and 20% triol-G400 solution exhibited positive brightness retention of 78% and 89%, respectively, the combination of 20% PEG-400 and 10% 1-octadecanol rendered the most significant photostability to the wood surface. Almost no change in brightness was observed. Color stabilization of wood by these treatments were also found (Fig. 6). In these studies, the most effective treatment for color and brightness stabilization was the combination of PEG-400 and 1-octadecanol, followed by triol-G400, and finally by 1-octadecanol and PEG-400.

Wood Surface Treated with Film-Forming Finishes

Changes in brightness and color of wood coated with different film-forming finishes following ultraviolet irradiation are shown in Figures 7 and 8. Wood finished with cellulose nitrate showed more severe discoloration than did untreated wood, indicating the instability of cellulose nitrate and showing that this finish cannot be used for exterior coatings. For wood coated with either phenolic varnish or polyurethane, a slight protection against

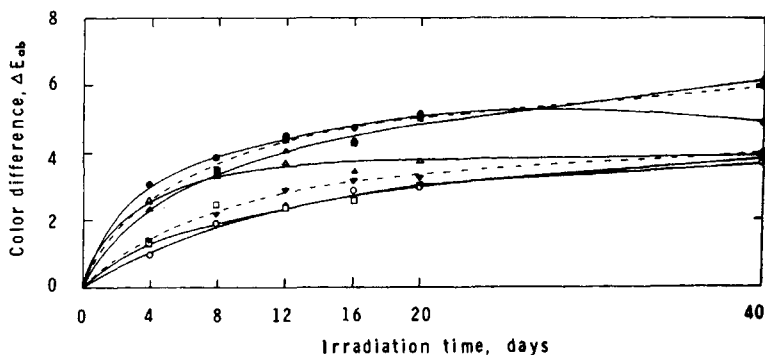


Fig. 6. Change in color of irradiated southern yellow pine treated with penetrating finishes: (Δ) 20% triol-G400; (\blacktriangle) 20% PEG-400; (\blacksquare) 10% PEG-400; (\bullet) 10% octadecanol; (\circ) 20% PEG-400 + 10% 1-octadecanol; (\square) 10% PEG-400 + 10% octadecanol; (\blacktriangledown) PEG-400 + 5% octadecanol.

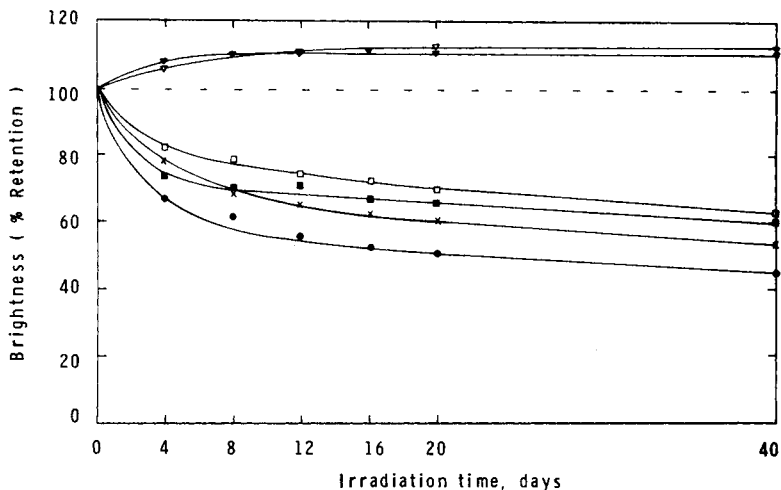


Fig. 7. Change in brightness of UV-irradiated southern yellow pine coated with nitrocellulose (●), phenolic varnish (■), polyurethane (□), homopoly(HMHBP) (▼), and copoly(HMHBP) (∇): (x) control.

ultraviolet irradiation was found. The outstanding performance of homopoly(HMHBP) and copoly(HMHBP) was very apparent. The brightness retentions of wood coated with the homopolymer or copolymer was around 110% and the color difference ΔE_{ab} only reached about 6 CIE-LAB color space.

Based on these findings, it is apparent that wood treated with PEG-400, triol-G400, homopoly(HMHBP), and copoly(HMHBP) exhibits positive stabilization effects against ultraviolet irradiation. It was expected that the control of discoloration would be more effective if homopoly(HMHBP) or copoly(HMHBP) were applied to a wood surface that had been pretreated with PEG-400 or triol-G400. This combined treatment actually stabilized the wood surfaces noticeably against ultraviolet irradiation (Figs. 9 and 10). In effect, wood treated with triol-G400 and copoly(HMHBP) exhibited an

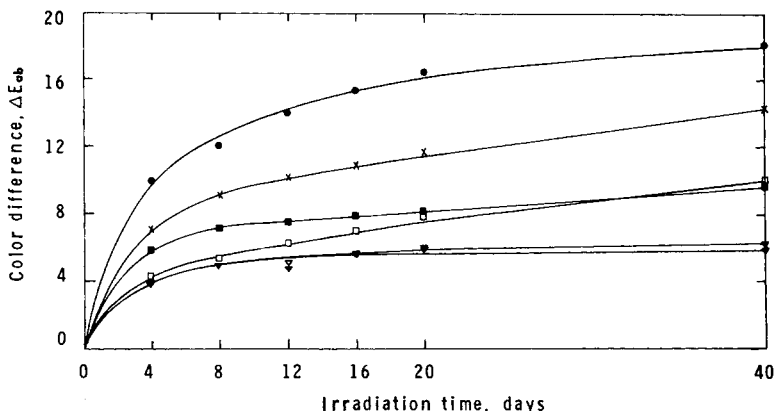


Fig. 8. Change in color of UV-irradiated southern yellow pine coated with nitrocellulose (●), phenolic varnish (■), polyurethane (□), homopoly(HMHBP) (▼), and copoly(HMHBP) (∇): (x) control.

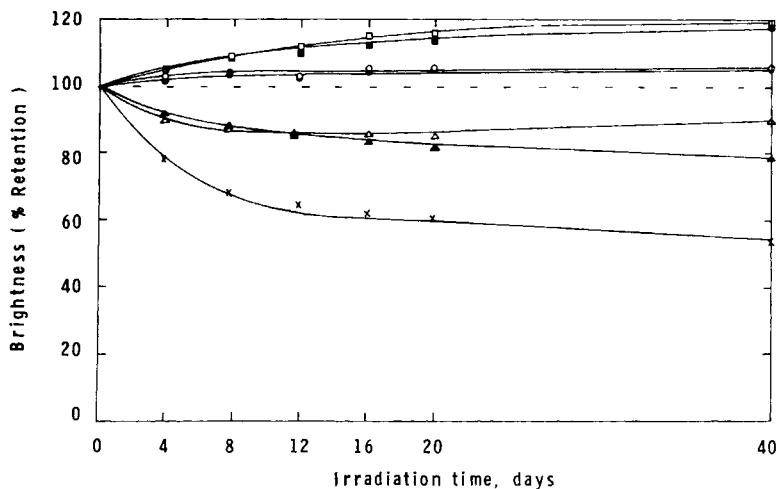


Fig. 9. Change in brightness of irradiated southern yellow pine treated with PEG (▲), triol (△), PEG + homopoly(HMHBP) (■), PEG + copoly(HMHBP) (□), triol + homopoly(HMHBP) (●), and triol + copoly(HMHBP) (○); (x) control.

excellent photostability against degradation, i.e., the brightness retention was 105% and the color difference varied only 3.6 CIE-LAB color space. Another beneficial effect was that surfaces treated with homopolymer or copolymer helped reduce the leach problem of triol-G400 or PEG-400 for wood surfaces, thus prolonging the long-term photostabilization effect.

The formation of hydroperoxides has been clearly demonstrated as an important intermediate during photodegradation.¹⁶ Because of this, we speculated that the stabilization effect of the copolymer would be further en-

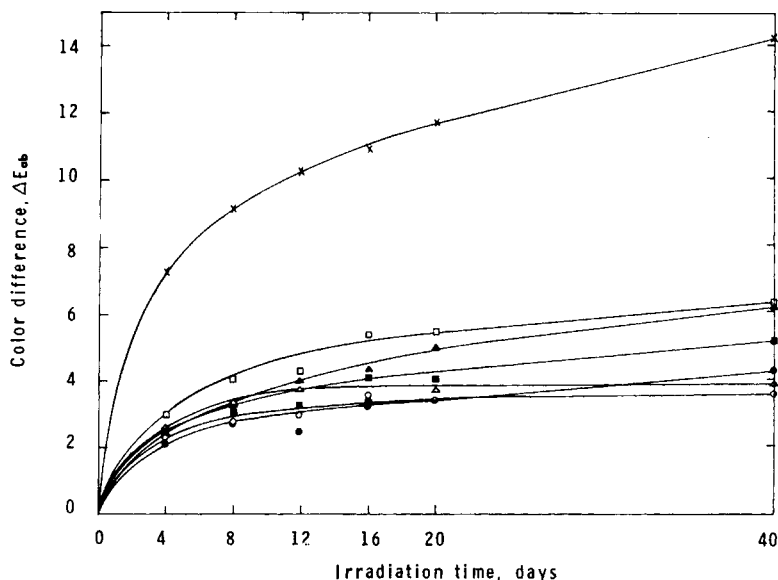


Fig. 10. Change in color of irradiated southern yellow pine treated with PEG (▲), triol (△), PEG + homopoly(HMHBP) (■), PEG + copoly(HMHBP) (□), triol + homopoly(HMHBP) (●), and triol + copoly(HMHBP) (○); (x) control.

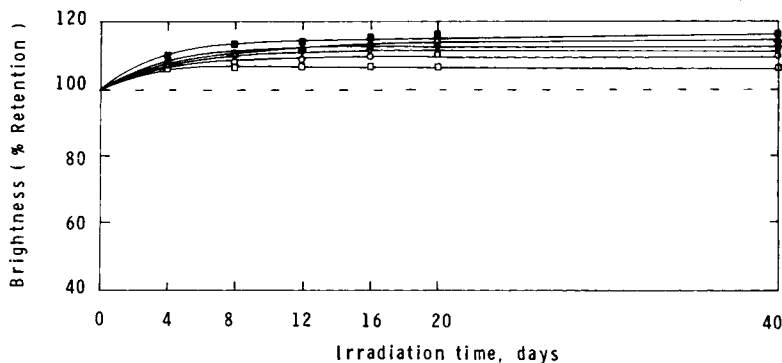


Fig. 11. Change in brightness of irradiated southern yellow pine coated with copoly(HMHBP) containing different UV stabilizers: (▽) copoly(HMGBBP); (□) copoly(HMHBP) + BHT; (■) copoly(HMHBP) + Mark-1409; (○) copoly(HMHBP) + Tinuvin 770; (●) copoly(HMHBP) + Irganox 1010; (△) copoly(HMHBP) + DABCO.

hanced by the addition of other stabilizers or antioxidants. Several ultraviolet stabilizers (Table I) were incorporated into the copolymer to see whether any synergistic effects of photostabilization could be achieved. As seen in Figures 11 and 12, there were no noticeable differences in brightness of wood treated with copolymer(HMHBP) containing different stabilizers. The only synergism observed was from wood treated with copoly(HMHBP) with added 2,6-di-*tert*-butyl-4-methylphenol (BHT).

Scanning Electron Microscopic (SEM) Studies

The transverse section of wood (i.e., southern yellow pine) is a simple and homogeneous structure composed of wood tracheids and only a relatively small amount of parenchyma cells. When unprotected wood transverse section specimens were exposed to ultraviolet light for 1000 hrs, noticeable surface deterioration was found.³ A scanning electron micrograph of a transverse earlywood surface of wood coated with homopoly (HMHP) before exposure is shown in Figure 13. When the specimen was exposed to ultra-

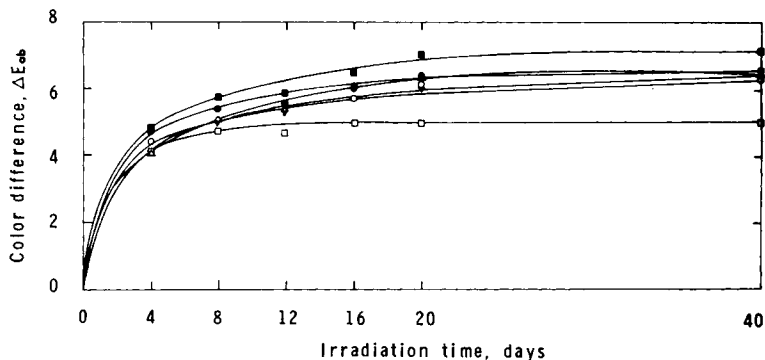


Fig. 12. Change in color of irradiated southern yellow pine coated with copoly(HMHBP) containing different UV stabilizers. (▽) copoly(HMHBP); (□) copoly(HMHBP) + BHT; (■) copoly(HMHBP) + Mark-1409; (○) copoly(HMHBP) + Tinuvin 770; (●) copoly(HMHBP) + Irganox 1010; (△) copoly(HMHBP) + DABCO.

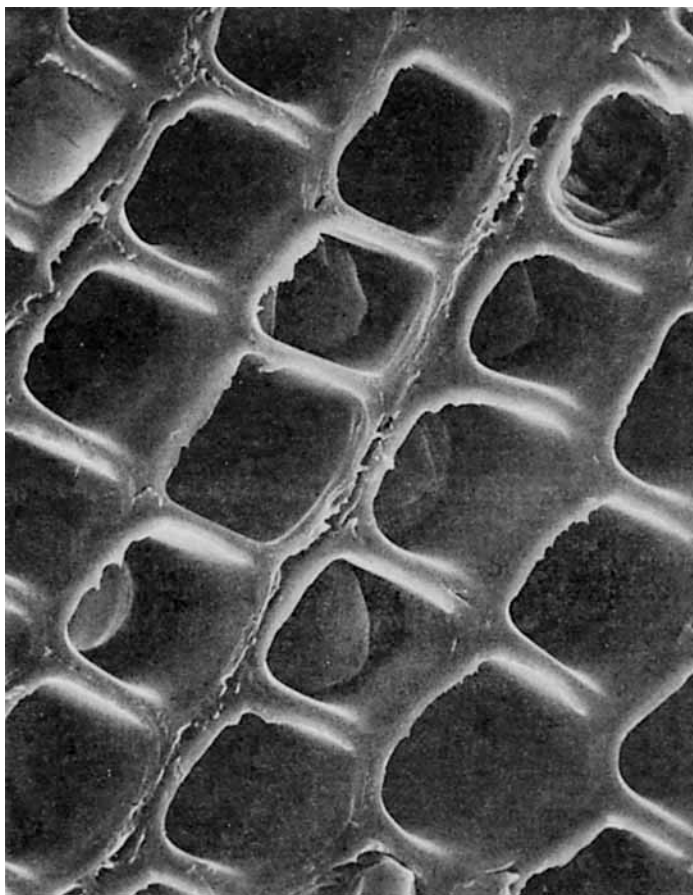


Fig. 13. SEM micrograph of transverse section early wood of southern yellow pine coated with homopoly(HMHBP) ($\times 250$).

violet light for 1000 h, there was no noticeable surface deterioration of wood substances and homopolymer was observed from the SEM micrographs. There was some degradation of the homopolymer after 2000 h of exposure (Fig. 14), but the underlying wood cell walls were intact. Similar results were observed from wood surfaces coated with copoly(HMHBP).

Infrared Spectroscopic Examination

As demonstrated in a previous paper,¹⁷ the most evident changes in the infrared spectrum of an unprotected wood surface after ultraviolet light irradiation are a decrease in intensity of the absorption bands at 1510 and 1265 cm^{-1} , which are the characteristic absorptions of lignin, and the noticeable increase in intensities of the absorption band near 1735–1720 cm^{-1} region, which is due to the carboxyl and/or carbonyl groups generated in cellulose as well as in lignin. The IR spectra of southern pine wood coated with a cellulose nitrate film showed a decrease in intensity of typical lignin absorption (1510 and 1265 cm^{-1}) and an increase in intensity of bands near 1735–1720 cm^{-1} region (resembling the change of untreated wood), indi-

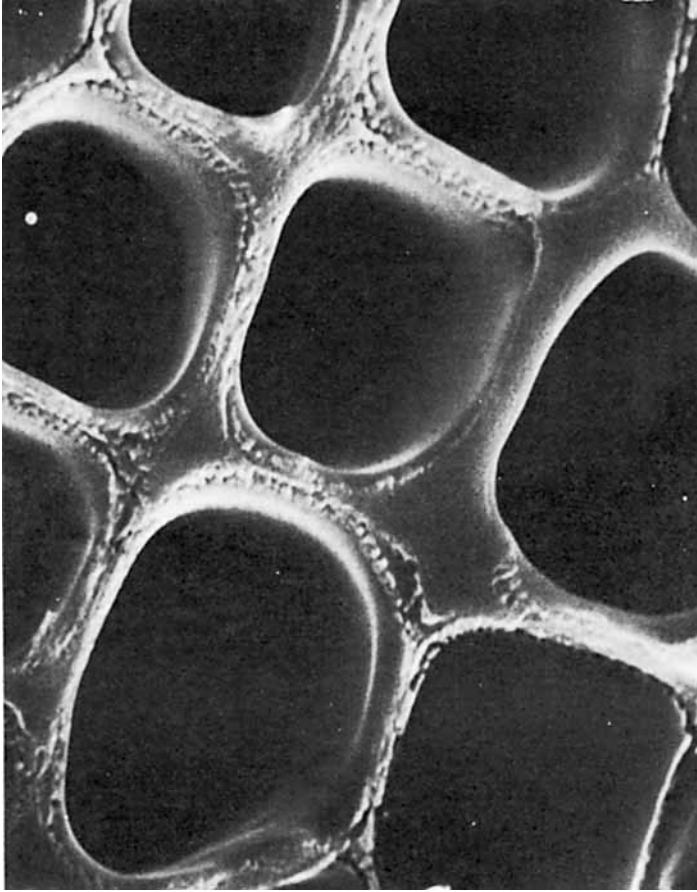


Fig. 14. SEM micrograph of transverse section earlywood of southern yellow pine coated with homopoly(HMHBP), irradiated with ultraviolet light for 2000 h ($\times 500$).

cating that cellulose nitrate cannot protect wood from ultraviolet irradiation (Fig. 15). This fully supports the brightness and color measurement studies discussed earlier.

By contrast, the outstanding performance of copoly(HMHBP) for protecting the wood surface against ultraviolet light can be seen from its IR spectra (Fig. 16). After 10 days of ultraviolet light exposure, the IR spectrum was nearly unchanged. After 40 days exposure, the decrease in intensity of the absorption bands at 1510 and 1265 cm^{-1} bands and the increase in intensities at 1735 and 1720 cm^{-1} were of no consequence. Quantitative determination of the lignin content of the ultraviolet-light-treated wood can be measured using a calibration curve that has been discussed in detail in a previous article.¹⁷ Using this technique, the residue lignin content of protected wood was found to be about 25%, suggesting that the degree of photodegradation of wood components, especially lignin, was reduced and, thereby, the formation of chromophoric groups was subdued.

The susceptibility of clear coating agents to photodegradation and loss of cohesion between coating agents and wood surfaces are generally recognized as ones of the serious limitations to their use. Therefore, coating

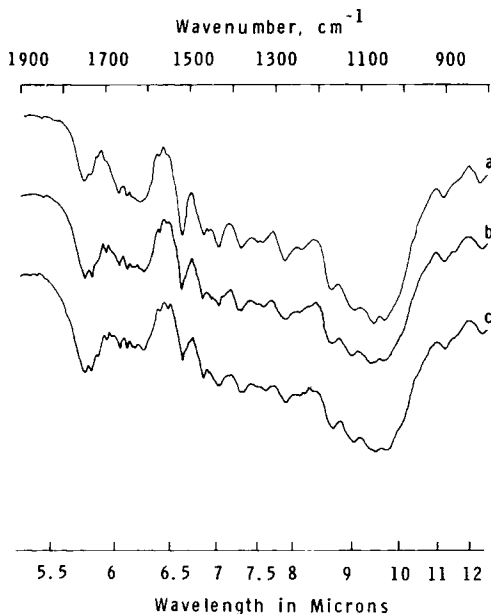


Fig. 15. Infrared spectra of southern yellow pine irradiated behind the nitrocellulose film: (a) control; (b) 4 days; (c) 10 days.

agents with high stability against ultraviolet light and with capability of screening of ultraviolet light are a prerequisite if the coatings are to be used as protective agents against photodegradation. The infrared spectra of copoly(HMHBP) after different periods of ultraviolet light irradiation showed that there was no modification of absorption bands, and absorption intensities were nearly identical to that of nonirradiated samples (Fig. 17). It is apparent that the copolymer used in these studies is very photostable.

Ultraviolet Visible Spectroscopy Examination

In a previous paper,¹⁷ we reported that water-soluble low molecular weight degradation products from ultraviolet light irradiated wood can be detected by using an ultraviolet spectrophotometer. It has been established that the concentration of degradation products is directly proportional to the intensity of absorption intensity. Since little chemical changes have been found in the IR spectra of wood underneath the copoly(HMHBP) film, it was expected that the amount of degradation products generated from wood surfaces would be small or insignificant. The differential ultraviolet absorption spectra of an aqueous solution extracted from irradiated wood underneath the copolymer film (Fig. 18) showed that, after 20 days of exposure, the optical density at 276 nm (0.166) in the spectrum of the wood extract was far lower than that of an extract from unprotected wood (0.648). This strongly suggests that relatively small amounts of water-soluble degradation products were formed due to the ultraviolet irradiation of wood coated with copoly(HMHBP).

Thermal Analysis of Coating Films

In general, photodegradation occurring on coating films results in the reduction of the molecular weight of the polymer of the film and changes in physical and mechanical properties. At the same time, the oxygen containing impurities, such as hydroperoxides and carbonyl that are being formed, are both sensitive to light. Their presence on the wood surface will accelerate and enhance degradation. If the chemical and physical properties of polymers were deteriorated due to ultraviolet degradation, the variations of thermal properties could be detected from the DSC. Figure 19 shows the DSC thermograms of irradiated and nonirradiated copoly(HMHBP) films.

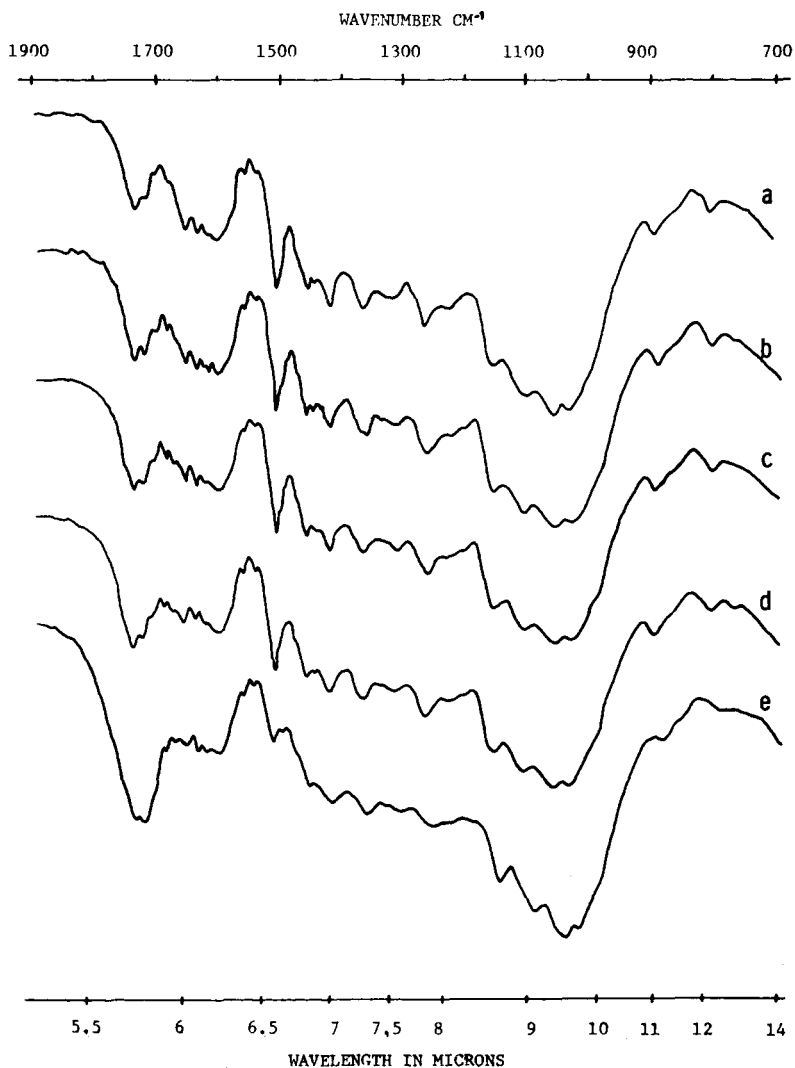


Fig. 16. Infrared spectra of southern yellow pine irradiated behind the copoly(HMHBP) film: (a) control; (b) 10 days; (c) 20 days; (d) 40 days; (e) 40 days without film.

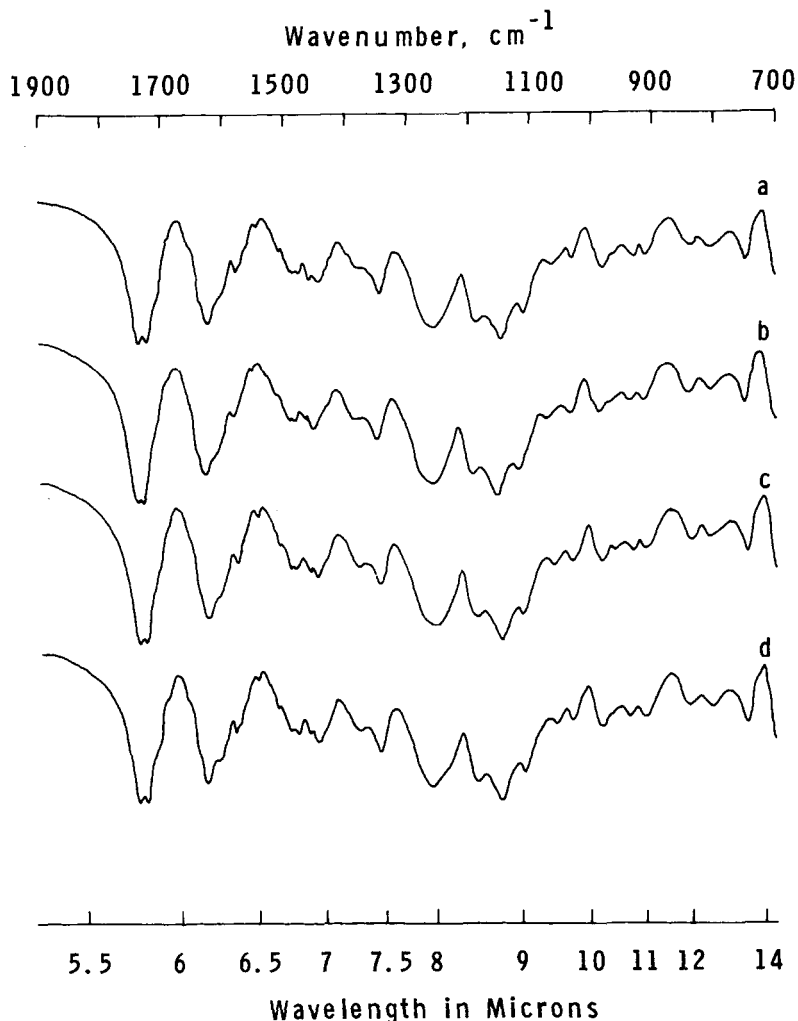


Fig. 17. Infrared spectra of irradiated copoly(HMHBP): (a) control; (b) 4 days; (c) 10 days; (d) 40 days.

It is evident that no significant change occurred in the DSC curves and even the glass transition temperature remained steady. This study demonstrates the excellent photostability of copoly(HMHBP), which is in agreement with the results concluded from the UV and IR spectroscopic studies.

Chemistry of Protection

In theory, the stabilization of organic polymers (e.g., wood) against photooxidation or weathering involves the retardation or elimination of primary photochemical process. Accordingly, possible stabilization to light can be achieved by adding ultraviolet screeners, excited state quenchers, free radical scavengers, and/or hydroperoxide decomposers, to the polymer films on wood surfaces, and by the alteration of chromophoric configurations to eliminate their capability to absorb light.

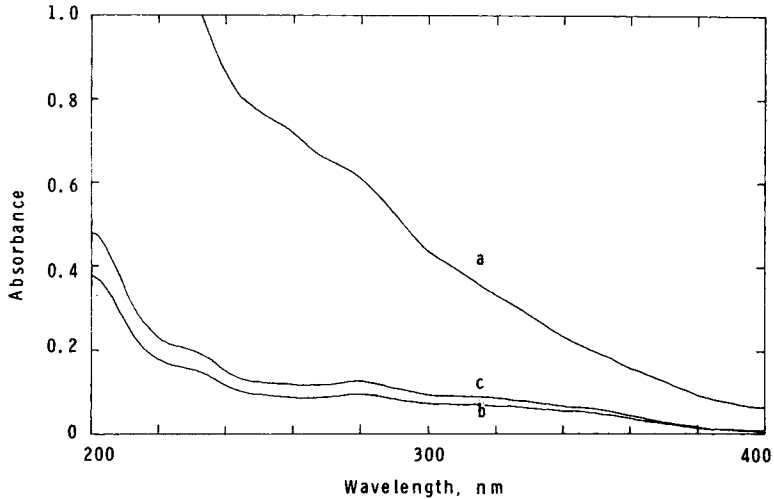


Fig. 18. Differential UV absorption spectra of water-soluble fraction of southern yellow pine behind a copoly(HMHBP) film, irradiated with UV light ($\lambda > 220$ nm) for 20 and 40 days: (a) unprotected wood for 20 days; (b) protected wood for 20 days; (c) protected wood for 40 days.

The remarkable performance of triol-G400 and PEG-400 against discoloration indicates that these compounds are suitable ultraviolet light stabilizers for wood. Although triol-G400 and PEG-400 do not absorb light, they may deactivate the photoexcited chromophoric groups in wood before any photochemical reactions can take place. The deactivation of photoexcited chromophores, which are responsible for photoinitiation, is achieved by an energy transfer process.¹⁸ The transfer of effective energy from the excited chromophoric groups in wood to the triol-G400 or PEG-400 can proceed through a system which involves the formation of hydrogen bonds between triol-G400 or PEG-400 and excited wood molecules. The more efficient photoprotective ability of triol-G400 is attributed to the number of available sites for the formation of hydrogen bonds through which the energy transfer can occur.

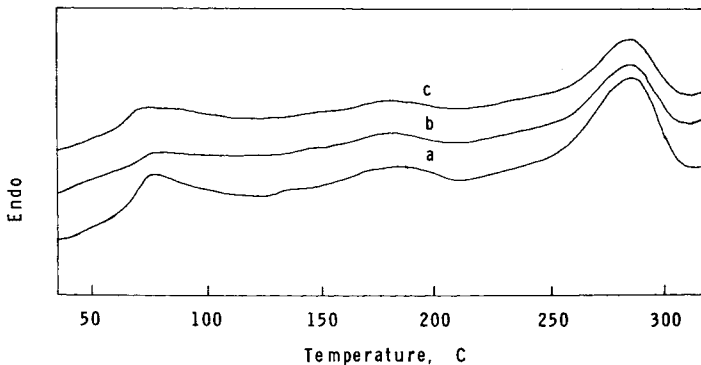
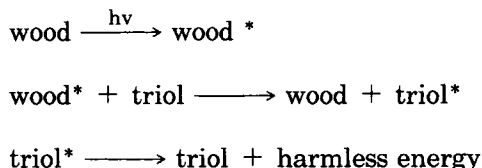


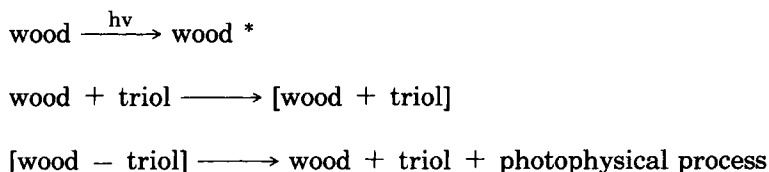
Fig. 19. DSC thermograms of irradiated copoly(HMHBP): (a) control; (b) 10 days; (c) 40 days.

The possible processes for the deactivated excited chromophores are shown in the following two routes: (1) Energy transfer resulting in a non-reactive triol-G400 or PEG-400 molecule:



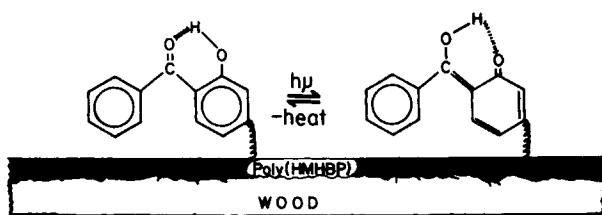
where * denotes excited state.

(2) Formation of an excited state complex that undergoes other photo-physical processes:



where * and [] denotes excited state and complex, respectively.

Of the many known ultraviolet absorbers, 2,4-DHBP is the most frequently used in commercial practice.¹⁹ The photochemistry of the *o*-hydroxy benzophenone has been extensively reported by many workers.²⁰⁻²⁵ It is well known that 2,4-DHBP dissipates its absorbed energy by a mechanism which involves the formation of hydrogen bond between hydroxyl and carbonyl groups. In essence, the polymeric ultraviolet light stabilizers, namely, poly(HMHBP) and its copolymer, contain an *o*-hydroxy benzophenone side chain attached to the backbone of the macromolecule. When these polymers are applied to the wood surface, the following "ketone-enol tautomerism" action provides a facile pathway for dissipation of absorbed energy:



Scheme 2

After absorption of ultraviolet light, photoexcited poly(HMHBP) dissipates its excited energy by a mechanism that involves the reversible formations of a six-member hydrogen bonded ring. This configuration allows energy transfer and hydrogen transfer, and eventually allows the *o*-hydroxyl benzophenone molecules to return to the ground state with release of relatively harmless thermal energy. As a consequence, the photo-stabilization of wood surface is due to the dissipation of the harmful energy through poly(HMHBP) and its copolymers.

The action of antioxidants is to inhibit oxidation of reactions promoted by oxygen or peroxides. However, most of the antioxidants absorb light in the region 250–400 nm.²⁶ Hence, they may be photolyzed or may be sensitized polymers for photochemical degradation. When 2,6-di-*tert*-butyl-4-methylphenol (BHT) was used as an antioxidant, however, a protection effect was observed. It is quite possible that the polymeric coating protects BHT from degradation during ultraviolet irradiation, and BHT concurrently scavenges free radicals or decomposed hydrogen peroxide to achieve an enhanced photostabilization effect.

CONCLUSIONS

The adverse consequences of ultraviolet light irradiation on wood surfaces are discoloration, chemical modification, and deterioration of the ultrastructure of cell walls. This detrimental photo degradation effect on wood surfaces can be reduced or prevented by either treating them with penetrating chemicals such as triol-G400, PEG-400, 1-octadecanol, and the combinations of coating them with polymeric clear finishes, such as poly(HMHBP) and its copolymer with alkyl methacrylate, containing an internal ultraviolet absorber.

Of the penetrating finishes employed in this study, triol-G400 was the most potential chemical agent to prevent discoloration of wood surfaces. Poly(HMHBP) and its copolymers proved to be good protective agents against photodegradation of wood. In addition to the positive photoprotective effects, experimental results also showed that poly(HMHBP) was quite stable and resistant to photodegradation. The combination of BHT with poly(HMHBP) offers enhanced protection against photodegradation. It is expected that when polymeric ultraviolet stabilizers are used in conjunction with clear coatings, they will make a potential and important contribution to photostabilization of wood and wood surfaces.

This study was supported in part by cooperative research funds provided by the Forest Products Laboratory, USDA Forest Service, Madison, Wisconsin, and this support is gratefully acknowledged.

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Received May 10, 1984

Accepted August 15, 1984