Photostability of Wood Surfaces Esterified by Benzoyl Chloride

K. K. Pandey, N. Chandrashekar

Institute of Wood Science and Technology, 18th Cross Malleswaram, Bangalore 560003, India

ABSTRACT: The photostabilization of wood surfaces is desirable to enhance the life of wood under exterior use and to improve the performance of clear coatings on wood surfaces. Chemical modification of wood has been found effective in upgrading properties such as biological durability and dimensional stability and has been suggested as a potential way for inducing photostability on wood surfaces. In this study, the photostability of chemically modified wood was assessed under accelerated weathering conditions. Wood specimens of *Pinus roxburghii* (Chir pine) were esterified with benzoyl chloride to 19.5 wt % gain and exposed to a xenon arc light source in a Weather-O-Meter for different periods ranging from 0 to 500 h. The irradiated samples were analyzed for color changes and chemical changes. The analysis of color changes in wood surfaces by ultraviolet–visible irradiation was carried out with a color measuring (CIELAB) system, and chemical changes were characterized with fluorescence and Fourier transform infrared spectroscopy. The esterification of wood by benzoyl chloride suppressed the color changes (photodiscoloration) due to irradiation. Modification also reduced the lignin degradation and generation of carbonyl groups on the surface of the irradiated wood. The fluorescence emission spectra of irradiated unmodified wood showed a large reduction in intensity and a large redshift in the emission maximum, whereas modified wood showed only a small change in fluorescence intensity on irradiation. The results show that the esterification of wood with benzoyl chloride was effective for the photostabilization of the wood polymers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2367–2374, 2006

Key words: esterification; fluorescence; FTIR; photodegradation; weathering; wood

INTRODUCTION

Wood surfaces exposed outdoors are subject to rapid photodegradation due to the delignification and depolymerization of carbohydrates.[1–3] Wood is a lignocellulosic macromolecule consisting mainly of cellulose, hemicellulose, and lignin. All of the constituent biopolymers of wood have reactive —OH groups, which are hydrophilic in nature; this results in dimensional instability and makes wood susceptible to microbial attack. In outdoor applications, when it is used above ground, wood is susceptible to degradation by a complex combination of chemical and physical factors; this is called *weathering*.[1–3] Degradation is a result of the absorption of ultraviolet–visible (UV–vis) light by wood constituent polymers that initiate photochemical reactions that result in the photocleavage of some of the chemical bonds. All of the chemical constituents of wood are susceptible to degradation by sunlight. The quantum energies associated with light are sufficient to break many of the chemical bonds present in the wood constituents. This results in the physical deterioration, discoloration, surface roughening, cracking, and damage of the microstructure. Weathering affects the physical and mechanical properties of wood and also results in premature coating failure. As a result of weathering, a huge quantity of wood is degraded and requires frequent replacement and refinishing.

Weathering deterioration also occurs underneath clear finishes and affects coating adhesion due to the photodegradation of wood surfaces, which results in coating failure. Ultraviolet (UV) light penetrates the clear coating and degrades the wood under it. This results in the delignification, discoloration, and degradation of the wood, which weakens the coating adhesion. Therefore, the wood under clear coatings needs to be stabilized against photodegradation to enhance the life of such clear coatings. Because weathering deteriorations are chemical in nature, it should be possible to eliminate it or decrease their rate by the modification of the basic chemistry of the cell-wall polymers of wood.[2,4,5] The development of pretreatment and chemical modifications for the stabilization of timber surfaces against weathering has generated considerable interest.[2,5]

The chemical modification of wood, in which chemical moieties form covalent linkages with hydroxyl groups in lignin and carbohydrates, offers potential as a way to upgrade wood properties such as biological durability and dimensional stability and may also provide weather resistance in wood.[5] Wood can be modified as esters (e.g., by acetylation, phthalylation, reaction with acid chloride and carboxylic acids), isocynates, acetals, ethers, epoxides, and so on with appropriate reagents.[4,6] These modifications enhance the dimensional stability and decay resistance of wood. However, the assessment of the photostability of chemically modified wood has received less attention. Some types of chemical modification of wood have been shown to be effective in reducing weathering deterioration under natural and accelerated weathering conditions.[4,5,7–14]

In this study, we carried out accelerated weathering experiments on *Pinus roxburghii* (Chir pine) wood surfaces esterified by benzoyl chloride. Modified and unmodified wood specimens were exposed to a UV–vis xenon source, and exposed surfaces were analyzed for color and chemical changes. Fluorescence and Fourier transform infrared (FTIR) spectroscopy were used to characterize the chemical changes on the wood surfaces caused by the weathering of unmodified and esterified wood. Fluorescence spectra of esterified wood are reported for the first time. Because of its high sensitivity, the fluorescence spectroscopic technique is an effective tool for measuring chemical changes that may occur due to modification and/or weathering deteriorations. The results presented in this article demonstrate the effectiveness of this technique to assess levels of chemical modification and weathering deteriorations.

EXPERIMENTAL

Chemical modification by benzoyl chloride

Wood specimens of *P. roxburghii* measuring 135 × 45 × 4 mm (Longitudinal × Radial × Tangential) were extracted with a mixture of ethanol/benzene (ratio = 1 : 2) for 6 h in a Soxhlet apparatus followed by extraction with ethanol for 4 h. Extracted samples were then oven-dried at 100–105°C for 12–15 h.

Extracted wood blocks were modified with benzoyl chloride (100 mL) in pyridene (500 mL) at 110°C for 4 h and were subsequently extracted with acetone to remove the unreacted benzoyl chloride and oven-dried to determine weight percentage gain (WPG). Thus, modified wood specimens with an average WPG of 19.5 ± 2.1 were obtained and exposed to the xenon source.

Accelerated weathering experiments

The photostability of benzoylated wood specimens was assessed under artificial accelerated weathering

conditions. Modified samples and unmodified samples (controls) were exposed to artificial accelerated weathering up to 500 h. An accelerated light-fastness test of the specimens was conducted in a Weather-O-Meter (Xenotest 150S, M/S ATLAS Instruments, Linsengericht, Germany). The specimens were exposed to a 1000-W xenon arc light source at a chamber temperature of 30°C and at 65% relative humidity. The samples were fixed in a stainless steel holder and rotated around the fixed xenon light source. The samples were removed from the Weather-O-Meter at regular intervals and analyzed for color and chemical changes. Three samples of each exposure period were obtained.

Color measurements

Changes in the color of the wood surfaces due to irradiation were measured with a color measuring system [Hunterlab Ultrascan(R) XE model, Reston, VA; d/8° measuring geometry, 10° standard observer, D65 standard illuminant, xenon flash lamp source, CIELAB system]. CIELAB *L**, *a**, *b**, and Δ*E** parameters were measured at six locations on each specimen, and average values were calculated. In the CIELAB system, the *L** axis represents the lightness [*L** varies from 100 (for white) to 0 (for black)], and *a** and *b** are the chromaticity coordinates (+*a** is for red, −*a** is for green, +*b** is for yellow, and −*b** is for blue). *L**, *a**, and *b** values were used to calculate the overall color change (Δ*E**) with the following equation:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \qquad (1)$$

where Δ*L**, Δ*a**, and Δ*b** are the differences in the initial and final values (before and after UV irradiation) of *L**, *a**, and *b**, respectively.

Measurement of the fluorescence and FTIR spectra

Steady-state fluorescence excitation and emission spectra were measured with an Edinburgh FS 900 spectrofluorometer (Livingston, UK). The fluorescence spectra were measured directly from the exposed wood surfaces in frontal mode under similar experimental conditions.

The FTIR spectra were obtained with a Nicolet Impact 400 spectrometer (Madison, WI). The top of the weathered surfaces were carefully removed with a razor blade, powdered, and analyzed by the direct transmission method (KBr pellet technique).[14,15] Spectra were measured at a spectral resolution of 4 cm^{-1}, and 64 scans were recorded per sample. Peak heights of the IR peaks were measured with OMNIC software (Nicolet, Madison, WI) according to previously published methods.[16] The heights of the peaks were measured from the baseline, which was constructed by the connection of the lowest data points on either side of

TABLE I
Color Changes in the Unmodified and Modified Wood Surfaces During Irradiation

Exposure duration (h)	Unmodified wood			Modified wood		
	L^*	a^*	b^*	L^*	a^*	b^*
0	76.5 ± 1.3	7.6 ± 0.9	25.6 ± 0.6	75.5 ± 1.2	5.4 ± 0.8	25.7 ± 1.2
20	67.2 ± 1.5	13.7 ± 0.8	41.5 ± 0.6	73.6 ± 1.6	5.2 ± 0.8	25.8 ± 1.1
50	58.5 ± 1.6	17.1 ± 0.8	39.4 ± 0.8	75.8 ± 1.2	4.5 ± 0.8	31.1 ± 0.8
100	56.3 ± 1.8	17.7 ± 1.0	37.9 ± 1.5	77.3 ± 1.5	3.3 ± 0.9	27.1 ± 1.3
200	49.9 ± 1.6	18.4 ± 1.0	33.1 ± 1.3	74.0 ± 1.2	3.5 ± 0.8	26.5 ± 0.8
300	45.9 ± 0.8	17.7 ± 0.5	30 ± 0.7	77.6 ± 0.7	3.2 ± 0.6	25.5 ± 0.6
400	43.0 ± 1.8	18.9 ± 0.8	27.9 ± 0.8	78.2 ± 0.6	2.7 ± 0.8	23.8 ± 0.9
500	38.9 ± 1.0	17.5 ± 0.7	24.3 ± 0.9	74.0 ± 1.2	2.4 ± 1.5	19.6 ± 1.0

Data are given as Mean $\pm$ Standard deviation.

the peak. A vertical line was then drawn from top of the peak to the x axis. The portion of the line between the top of the peak and the baseline represented the corrected peak height.

RESULTS AND DISCUSSION

Color changes

The color changes due to photoirradiation on the unmodified and modified wood surfaces of *P. roxburghii* are summarized in Table I. *P. roxburghii* was a light colored wood ($L^* = 76.5 \pm 1.3$). The color of the unmodified wood surfaces changed rapidly on irradiation. The color of the untreated specimens darkened on irradiation. The rapid color change due to irradiation of the unmodified wood surface was indicated by a decreasing value of L^* and an increasing value of a^* and b^* on exposure. ΔE^* increased rapidly with irradiation time, with the rate of change being very high at the initial stages of irradiation. The color changes on the wood surfaces were mainly due to the liberation of chromophoric carbonyl units as a consequence of the photodegradation of the wood constituents, mainly lignin.[2,3]

The esterification of wood with benzoyl chloride caused no significant change in the color of the wood. The color of the modified specimens remained almost unchanged on irradiation. The value of L^* decreased and ΔE^* increased rapidly with exposure duration in the unmodified wood, whereas there were only very small changes in the values of these parameters in the modified wood. L^* values remained almost constant in the modified wood. The parameter a^* increased on weathering in the unmodified wood, whereas its value decreased in the modified wood. There was only a slight increase in ΔE^* on irradiation in the modified wood. ΔE^* values for the unmodified (control) and modified wood surfaces are compared in Figure 1. This figure shows that the benzoylated wood worked effectively in to stabilize the wood color against photodegradation.

FTIR spectra

The effect of irradiation on the FTIR spectra of the unmodified *P. roxburghii* is shown in Figure 2. Changes in the chemical structure of the wood surfaces during irradiation in the unmodified wood were evident from the IR spectra. Analyses of the FTIR spectra showed a significant reduction in the intensity of the aromatic lignin C=C band (1511 cm^{-1}), which almost disappeared within a few hours of exposure. A rapid reduction in the intensity of the C=C band indicated modification in the lignin structure. This was accompanied by an increase in the intensity of carbonyl absorption in the 1734-cm^{-1} region and around 1650 cm^{-1}. A significant increase in the intensity of the 1650-cm^{-1} band indicated quinone formation during irradiation. This was combined with a loss of aromatic structures and the formation of conjugated
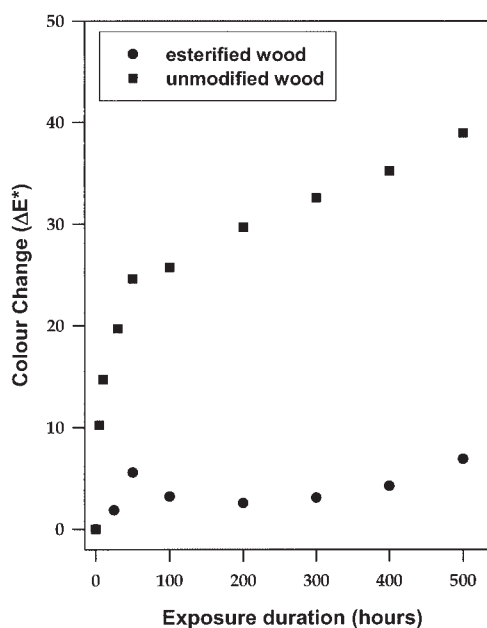

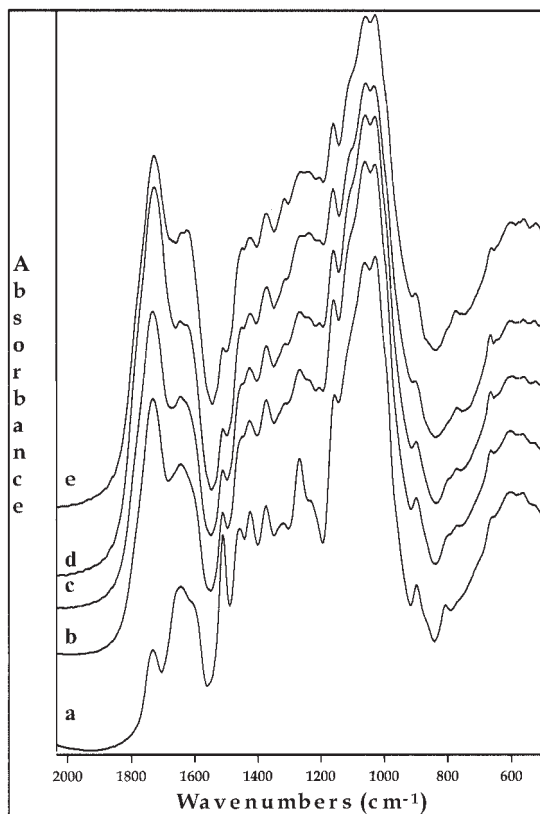**Figure 1** Comparison of ΔE^* values in (■) unmodified and (●) modified *P. roxburghii*.

Figure 2 FTIR spectra of unmodified *P. roxburghii* weathered for (a) 0, (b) 50, (c) 100, (d) 200, and (e) 500 h.

and nonconjugated carbonyls. The bands at 1734 and 1650 cm^{-1} were characteristic absorptions of carbonyl stretching vibrations of nonconjugated (in xylan) and conjugated (in lignin) esters and carboxylic acids,[15,17–20] and their concentration increased as carbonyl groups were liberated from lignin and/or carbohydrates due to chemical degradation. The influence of photoirradiation on the wood surfaces was quite rapid. Significant changes occurred within a few hours of irradiation.

A number of researchers have attempted to understand the mechanism of the degradation of wood,[2,3,21,22] pulp,[23–25] extracted lignin,[26] and lignin model compounds.[27] Despite extensive work, the precise mechanism and pathways involved in the photodegradation of wood are not yet completely understood. Photochemical reactions are initiated by the absorption of UV–vis light, mainly by lignin, which leads to the formation of aromatic and other free radicals.[3] These free radicals may then cause the degradation of lignin and the photooxidation of cellulose and hemicellulose. This results in the formation of colored unsaturated carbonyl compounds, which explains the color changes and the yellowing of wood surfaces. These photoinduced color changes (ΔE^*) correlate very well with the formation of carbonyl groups

and the degradation of lignin.[22,28] Lignin is a good light absorber, with absorptions up to 400 nm with a major peak at 280 nm.[3] Phenolic hydroxyl groups rapidly react with light to produce a phenolic radical, which in turn, transforms into *o*-quinonoide and *p*-quinonoide structures by demethylation or by the cleavage of the side chain[3] and the formation of carbonyl-based chromophoric groups.[24] The formation of quinone is combined with a loss of aromatic structures, which can be seen from a rapid decrease in the intensity of the 1511-cm^{-1} absorption and the formation of conjugated and nonconjugated carbonyls. An increase in the intensity of the 1650-cm^{-1} absorption with exposure duration indicates that the content of conjugated carbonyl or carboxyl groups, such as quinoid derivatives or ring-opened conjugated carboxylic acid, increases with the photooxidation of lignin.[29]

The chemical modification of wood by benzoyl chloride was indicated from the decrease in the intensity of the hydroxyl band, accompanied by increases in the intensities at 1724, 1601, 1453, 1272, and 710 cm^{-1} [Fig. 3(b)]. Benzoyl chloride reacted with the O—H group of wood to form an ester:
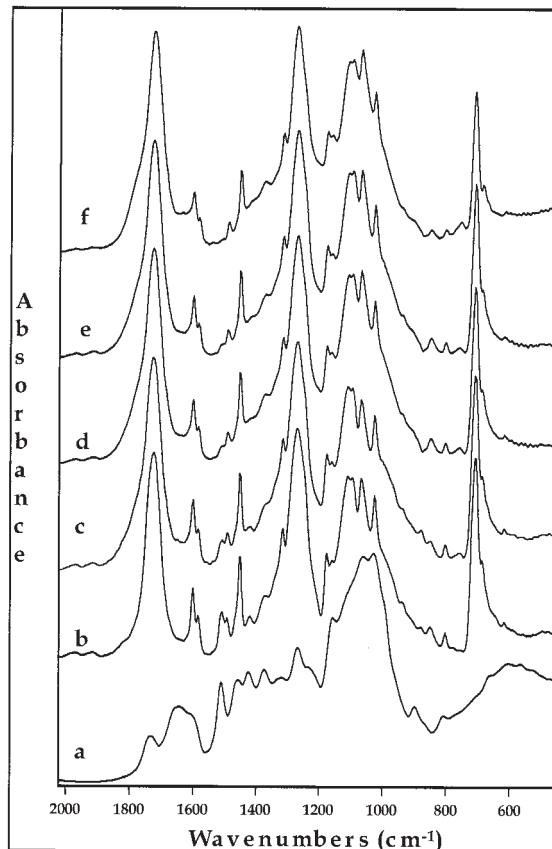

Figure 3 FTIR spectra of (a) unweathered and unmodified wood and modified *P. roxburghii* (19.5 WPG) weathered for (b) 0, (c) 50, (d) 100, (e) 200, and (f) 500 h.

The introduction of benzoyl groups resulted in an increase in the carbonyl stretching absorption around 1724 cm^{-1} and in bands characteristic of aromatic rings (1601, 1500, 1453, and 710 cm^{-1}) and a strong absorption at 1272 cm^{-1}. The major difference between the spectra obtained from the modified and unmodified wood was the presence of carbonyl peaks around 1724 and 1272 cm^{-1}. The intensity of the carbonyl peaks increased as WPG increased. This was accompanied by a rapid decrease in the intensity of the O—H band, which indicated the replacement of hydroxyl groups and the formation of esters. The ratio of the intensities of the carbonyl band (1724 cm^{-1}) to the hydroxyl band (3410 cm^{-1}), which was indicative of the degree of modification, increased with reaction time and/or WPG.

Figure 3 shows the effect of irradiation on the FTIR spectra of *P. roxburghii* wood surfaces modified by benzoyl chloride. Esterification of the wood with benzoyl chloride was effective in the photostabilization of the wood surfaces. The increase in absorption at 1734 cm^{-1} on irradiation in benzoylated wood was insignificant compared to that in unmodified wood, whereas the decrease at 1511 cm^{-1} was smaller than in the unmodified specimen. Similarly, the changes due to irradiation in the C—O group at 1272 and 710 cm^{-1} were insignificant. This indicated that benzoylated groups were not easily removed from wood during light irradiation. This also explained the very little color change in the modified wood due to irradiation. The color change in the unmodified wood was due to the formation of carbonyl groups, mainly because of lignin degradation, which was indicated by the increased intensity of the C=O band at 1734 cm^{-1} in the unmodified wood. In the modified wood, the esterified groups were more stable with weathering, which was indicated by the lack of significant change in the intensity of 1734-cm^{-1} band on irradiation. Although modified samples showed degradation of lignin on irradiation, the effect was much less pronounced than that of unmodified samples. The absorption of UV light by lignin resulted in the formation of aromatic and other free radicals, which triggered the further degradation of lignin, which resulted in the formation of colored unsaturated carbonyl groups. Phenoxy hydroxyl groups in lignin react with light to produce phenolic radicals. In the modified wood, these groups were blocked by the formation of more stable ester groups. The region of absorption of the benzoyl groups overlaps with that of lignin.[12] The introduction of benzoyl groups, therefore, may retard the formation of aromatic radicals and the degradation of lignin by
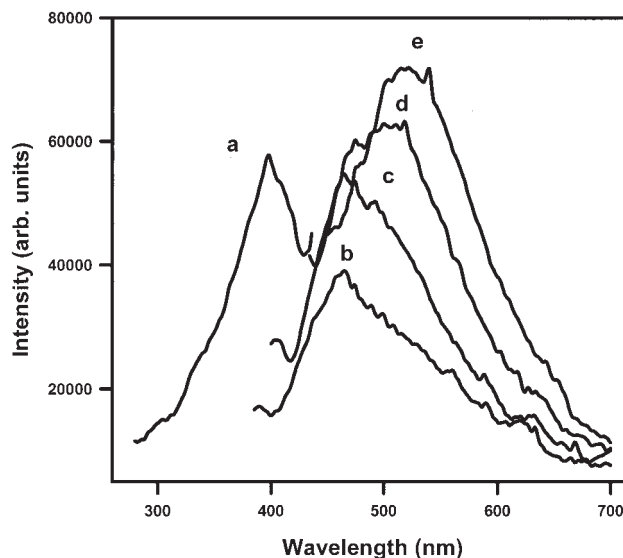
Figure 4 Fluorescence spectra of unmodified *P. roxburghii*: (a) excitation spectra at emission wavelength (λ_{em}) = 460 nm and emission spectra at λ_{ex} = (b) 360, (c) 380, (d) 400, and (e) 420 nm.

the absorption of UV light.[12] In an earlier work, Evans et al.[12] reported that the esterification of Scot pine by benzoyl chloride was effective at photostabilizing wood at a very high WPG (72%). They also reported that benzoylation of wood at very high weight gain caused the swelling of wood cell walls and a large loss in the tensile strength.[12] Therefore, the results of our study in which wood was modified to low WPG are encouraging. Only surface modification is important for weathering properties as most of the available/accessible hydroxyl groups present in the outer wood surfaces may have all reacted even at low weight gain.

Fluorescence spectra

The degradation of *P. roxburghii* wood surfaces was further studied with fluorescence spectroscopy. Although there are a few reports on the fluorescence spectroscopic studies of irradiated cellulose,[30,31] pulp, and paper,[32–35] such studies on irradiated solid wood are scant. To the best of our knowledge, fluorescence spectroscopy has been used for the first time in this study to characterize modified solid wood and to assess the photostability of weathered modified solid wood.

The fluorescence excitation and emission spectra measured from unmodified *P. roxburghii* are shown in Figure 4. Figure 4 shows broad excitation spectra with a maximum around 380–400 nm. The emission spectra showed excitation wavelength ($\lambda_{ex;}$) dependence. A broad spectrum with an emission peak around 450 nm with a shoulder at a longer wavelength (ca. 520 nm) was observed for $\lambda_{ex;}$ values less than 380 nm. The
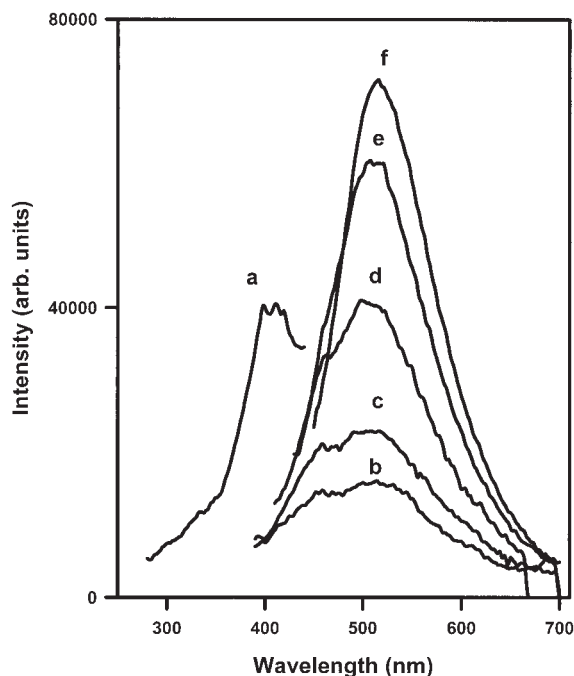
The effect of weathering on the emission spectra measured from unmodified wood surfaces of *P. roxburghii* with 370-nm excitation is shown in Figure 7. Photoirradiation resulted in a large and rapid decrease in the overall intensity, a broadening of the emission band, and a large shift in the emission maximum toward longer wavelengths. The intensity of the emission peak at 450 nm decreased rapidly, and the relative intensity of the longer wavelength component band increased on irradiation. The quenching of the intensity of the 450-nm band resulted in an apparent increase in the emission from the higher wavelength species, which may have been obscured in unirradiated wood. The decrease in the emission intensity may have been due to the formation of carbonyl groups as a result of lignin decay. Carbonyl groups generated during the photodegradation of wood surfaces act as fluorescence quenchers.[36] Fluorescence quenching follows a linear relationship with the relative concentration of carbonyl groups formed during photodegradation.[28] The decrease in the fluorescence intensity of the irradiated surfaces also supported the formation of quinones, which are generally nonfluorescent.[25] Similar results on the photoirradiation of high-yield pulps (pressure-ground wood and chemimechanical pulp) have been reported.[33,34]

Figure 5 Fluorescence spectra of esterified *P. roxburghii* (19.5 WPG): (a) excitation spectra at λ_{em} = 460 nm and emission spectra at λ_{ex} = (b) 350, (c) 370, (d) 390, (e) 410, and (f) 430 nm.

excitation with a longer wavelength (>400 nm) resulted in a reduction in the intensity of the 450-nm peak and an increased intensity of the longer wavelength component. The excitation with longer wavelength also resulted in a shifting of emission maximum to a longer wavelength (550 nm). The $\lambda_{ex;}$ dependence and the broad nature of the fluorescence spectra with a shoulder at longer wavelengths may have been due to the presence of many different chromophoric species that are present in such a complex wood material. The emission spectra of wood had contributions from both cellulose and lignin. However, the main contribution may have been from lignin,[35] which has more chromophoric groups present.

The excitation and emission spectra of benzoylated *P. roxburghii* (19.5 WPG) are shown in Figure 5. The emission spectra of modified wood showed two distinct maxima centered at 440 and 510 nm, which exhibited $\lambda_{ex;}$ dependence. The intensity of the peak centered at 450 nm decreased when the sample was excited at a longer wavelength, and that of the higher wavelength component (centered at 510 nm) increased. The effect of the degree of modification on the emission spectra is shown in Figure 6. The overall fluorescence intensity increased with increasing level of modification. Increasing WPG (modification) also resulted in an increasing intensity of the longer wavelength component. The ratio of the intensity of the 450- and 510-nm bands decreased with increasing WPG.
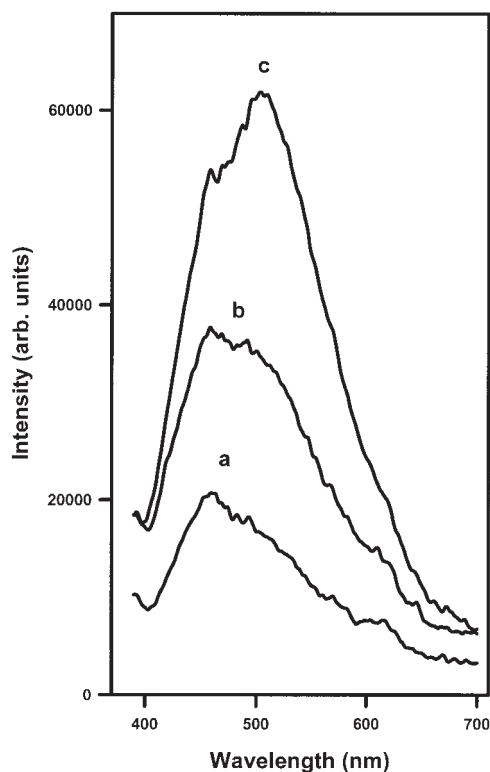

Figure 6 Emission spectra of *P. roxburghii* modified to different levels (WPGs): (a) unmodified wood, (b) wood modified to 7.5 WPG, and (c) wood modified to 19.5 WPG. λ_{ex} = 370 nm.

The effect of irradiation on the fluorescence spectra measured from the surfaces of esterified *P. roxburghii* is shown in Figure 8. λ_{ex} was 370 nm. The overall intensity first decreased slightly and then increased on further irradiation. Photoirradiation also resulted in the recovery of shorter wavelength components, which was indicated by an increase in the ratio of the intensity of the 450- and 510-nm components. The degree of change of the fluorescence intensity was much less that that of the unmodified wood. Our results from the fluorescence spectroscopic measurements for the characterization of chemical modification reactions and the assessment of their stability are encouraging. However, a more detailed study of modified wood in this aspect is needed to understand these changes.

CONCLUSIONS

By monitoring color changes and using fluorescence and FTIR spectroscopy, we examined the chemical modification of wood with benzoyl chloride and light stability of benzoylated wood. The color changes due to irradiation (photodiscoloration) on modified wood were much less than those of unmodified wood. Es-
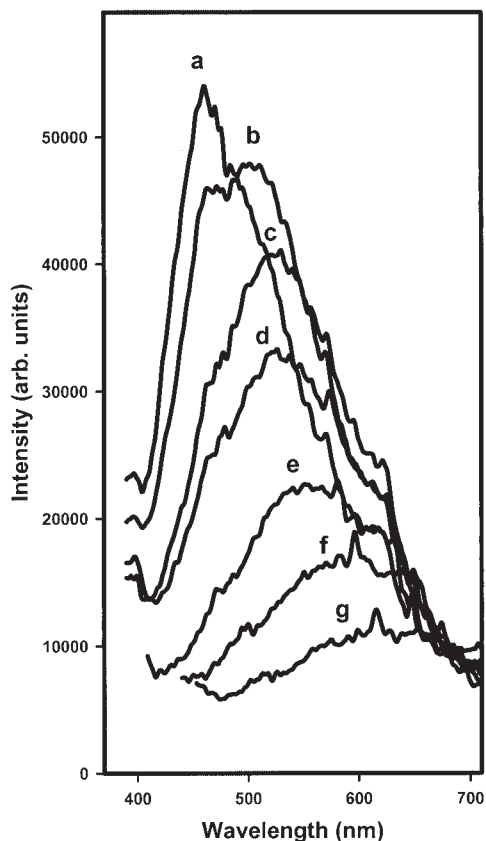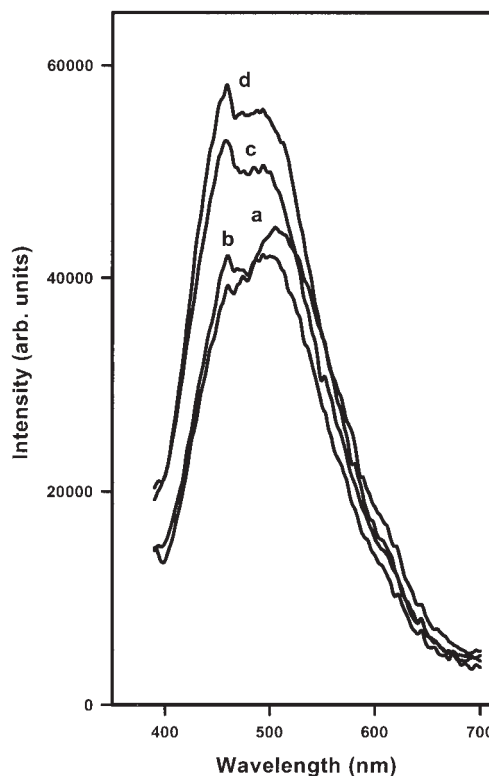
Figure 8 Fluorescence emission spectra of modified *P. roxburghii* (WPG = 19.5) weathered for (a) 0, (b) 100, (c) 400, and (d) 500 h. λ_{ex} = 370 nm.

terification of wood with benzoyl chloride reduced the lignin degradation and the generation of carbonyl groups on the surface of irradiated wood.

Unmodified wood gave a broad λ_{ex}-dependent emission band. Esterification by benzoyl chloride caused a strong increase in the fluorescence intensity and a shift in the emission maximum to a longer wavelength. The intensity of the shorter wavelength component decreased rapidly, whereas the emission of the higher wavelength component increased with increasing degree of esterification (WPG).

The photoirradiation of the unmodified wood resulted in the broadening of the emission band, a large reduction in the fluorescence intensity, and a large shift in the emission maximum to a longer wavelength. The irradiation of modified wood caused a small increase in the fluorescence intensity. Fluorescence and FTIR spectra measured from modified wood irradiated for different durations provided evidence of the photostabilization of benzoylated wood. Modified samples were less vulnerable to photodegradation than unmodified wood.

Figure 7 Fluorescence emission spectra of unmodified *P. roxburghii* weathered for (a) 0, (b) 10, (c) 20, (d) 30, (e) 75, (f) 200, and (g) 500 h. λ_{ex} = 370 nm.

course of this study. We also acknowledge Lohit K. for carrying out experiments related to chemical modification of wood.

References

1. Hon, D. N.-S.; Chang, S.-T. J Polym Sci Polym Chem Ed 1984, 22, 2227.
2. Feist, W. C.; Hon, D. N.-S. In The Chemistry of Solid Wood; Rowell, R., Ed.; American Chemical Society: Washington, DC, 1984; p 401.
3. Hon, D. N. S. In Wood and Cellulosic Chemistry; Hon, D. N. S.; Shiraishi, N., Eds.; Marcel Decker: New York, 1991; p 525.
4. Rowell, R. M. In The Chemistry of Solid Wood; Rowell, R., Ed.; American Chemical Society: Washington, DC, 1984; Chapter 4, p 175.
5. Plakette, D. V.; Dunningham, E. A.; Singh, A. P. In Chemical Modification of Lignocellulosic Materials; Hon, D. N. S., Ed.; Marcel Dekker: New York, 1996; Chapter 11, p 277.
6. Matsuda, H. In Chemical Modification of Lignocellulosic Materials; Hon, D. N. S., Ed.; Marcel Dekker: New York, 1996; Chapter 6, p 159.
7. Feist, W. C.; Rowell, R. M.; Ellis, W. D. Wood Fiber Sci 1991, 23, 128.
8. Imamura, Y. Wood Res 1993, 79, 54.
9. Owen, J. A.; Owen, N. L.; Feist, W. C. J Mol Struct 1993, 300, 105.
10. Plackett, D. V.; Dunningham, E. A.; Singh, A. P. Holz Roh Werkstoff 1992, 50, 135.
11. Evans, P. D.; Wallis, A. F. A;. Owen, N. L. Wood Sci Technol 2000, 34, 151.
12. Evans, P. D.; Owen, N. L.; Schmid; S.; Webster, R. D. Polym Degrad Stab 2002, 76, 291.
13. Ohkoshi, M. J. Wood Sci 2002, 48, 394.
14. Pandey, K. K.; Pitman, A. J. J Appl Polym Sci 2002, 85, 622.
15. Pandey, K. K. J Appl Polym Sci 1999, 71, 1969.
16. Pandey, K. K.; Pitman, A. J. Int Biodeterioration Biodegrad 2003, 52, 151.
17. Harrington, K. J.; Higgins, H. G.; Michell, A. J. Holzforschung 1964, 18, 108.
18. Faix, O. In Methods in Lignin Chemistry; Lin, S. Y.; Dence, C. W., Eds.; Springer-Verlag: Berlin, 1992; p 83.
19. Faix, O.; Bottcher, J. H. Holz Roh Werkstoff 1992, 50, 221.
20. Pandey, K. K.; Theagarajan, K. S. Holz Roh Werkstoff 1997, 55, 383.
21. Hon, D. N.-S.; Chang, S.-T. Wood Sci Technol 1982, 16, 193.
22. Muller, U.; Ratzsch, M.; Schwanninger, M.; Steiner, M.; Zobi., H. J Photochem Photobiol B 2003, 69, 97.
23. Bonini, C.; Auria, M. D'; Alessio, L. D'; Mauriello, G.; Viggiano, D.; Zimbardi, F. J Photochem Photobiol 1998, 118, 107.
24. Schmidt, J. A.; Heitner, C. J. Wood Chem Technol 1993, 13, 309.
25. Zhu, J. H.; Olmstead, J. A.; Grey, D. G. J. Wood Chem Technol 1995, 15, 43.
26. Bonini, C.; Auria, M. D'; Alessio, L. D'; Mauriello, G.; Viggiano, D.; Zimbardi, F. J Photochem Photobiol 1998, 118, 107.
27. Crestini, C.; Auria, M. D'. J Photochem Photobiol A 1996, 101, 69.
28. Pandey, K. K. Polym Degrad Stab 2005, 90, 9.
29. Chang, H. T.; Yeh, T. F.; Chang, S. T. Polym Degrad Stab 2002, 77, 129.
30. Tylli, H.; Forsskahl, I.; Olkkonen, C. J Photochem Photobiol A 1993, 76, 143.
31. Tylli, H.; Forsskahl, I.; Olkkonen, C. Cellulose 1996, 3, 203.
32. Davidson, R. S.; Dunn, L. A.; Castellan, A.; Nourmamode, A. J Photochem Photobiol A 1991, 58, 349.
33. Tylli, H.; Forsskahl, I.; Olkkonen, C. J. Photochem Photobiol A 1992, 67, 117.
34. Tylli, H.; Forsskahl, I.; Olkkonen, C. J Photochem Photobiol A 1995, 87, 181.
35. Castellan, H.; Choudhry, H.; Davidson, R. S.; Grelier, S. J Photochem Photobiol A 1994, 81, 117.
36. Olmstead, J. A.; Gray, D. G.. J Photochem Photobiol A 1993, 73, 203.