

Scanning electron microscope and infrared studies of weathering in Southern pine

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Abstract

Southern pine has been subjected to a variety of artificial weathering conditions and the wood surface analyzed using infrared spectroscopy and scanning electron microscopy (SEM). The effect of light on the weathering process is quite rapid; changes in functional groups on the wood surface, as monitored by infrared spectroscopy, occur within a few hours exposure. Light and water, both acting together, cause the greatest damage to the surface polymer structure, whereas water alone has very little effect on the chemistry of the surface. SEM data, however, show that water has a deleterious effect on the physical characteristics of the surface. Acetylation of the wood under mild conditions serves to protect the surface from the weathering effect of light and water. The extent of weathering is reduced by approximately 50%.

Introduction

The importance of wood as a versatile and attractive structural material has been recognized for centuries. However, in common with other biological materials, wood is susceptible to environmental degradation. When wood is exposed to the natural elements (e.g. air, water and light) as well as to man-made pollutants (e.g. toxic gases, acid rain, etc.), a complex series of physical and chemical changes occur in a process commonly described as weathering [1]. This degradation process often results in discoloration and in the physical deterioration of the wood surface. In particular, checks or cracks appear in the surface and the paint-holding characteristics of the wood decreases. Along with these changes in physical properties it has been established that some of the polymer constituents of wood are broken into smaller components, and the chemical nature of

the surface layers changes [1]. However, there is evidence to suggest that the primary effect of weathering is limited to the surface layers – although secondary chemical processes may, in certain instances, cause changes to occur relatively deep within the wood [2].

This paper describes studies of the surface features of Southern pine (*Pinus sp.*) carried out by means of electron microscopy and infrared spectroscopy, and of how the nature of the surface changes with varying conditions and with extent of weathering. Also reported are our studies of samples of Southern pine wood which were subjected to some of the same weathering conditions but which were previously acetylated as a means of protection from weathering effects.

The application of both scanning electron microscopy (SEM) and infrared spectroscopy to investigate surface features in wood samples is fairly well established [3,4]. However, in this paper the attempted correlation of the results from both techniques in an attempt to improve our understanding

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of the nature of the weathering process in wood is described.

Experimental

Samples of Southern pine wood were prepared, weathered and treated with acetylating agents at the Forest Products Laboratory in Madison, Wisconsin. The full weathering process comprised of continuous exposure in an Atlas Xenon Arc Weatherometer to UV light and bombardment by a water spray for 4 h per day, for the allotted time period. The UV light-only samples were subjected to continuous exposure to UV light for the appropriate periods. The water-only samples were continually sprayed with water for specific time periods. Samples were acetylated to approximately 20% weight gain using a method described previously [5].

A JEOL JSM 840A instrument was used for the electron microscopy. The wood samples were all radial cuts of Southern pine and were cut such that they had a viewing surface of approximately

1 cm². The sample was then attached to an aluminium specimen stub, the sides were painted with silver, and the surface coated with a thin layer of gold.

All infrared spectra were taken using a Mattson Sirius 100 spectrometer operating at 4cm⁻¹ resolution incorporating a Spectra Tech diffuse reflectance (collector) accessory unit.

Results

Infrared spectra

Untreated wood

Southern pine, a popular softwood used extensively in the building industry, is known to be subject to normal weathering when exposed outdoors [6]. The untreated wood is characterized by having a pale yellow-brown color. The infrared spectra of its surface shows a very strong, broad O-H stretching absorption centered at about 3400 cm⁻¹, a well defined absorption doublet arising from C-H stretching vibrations centered

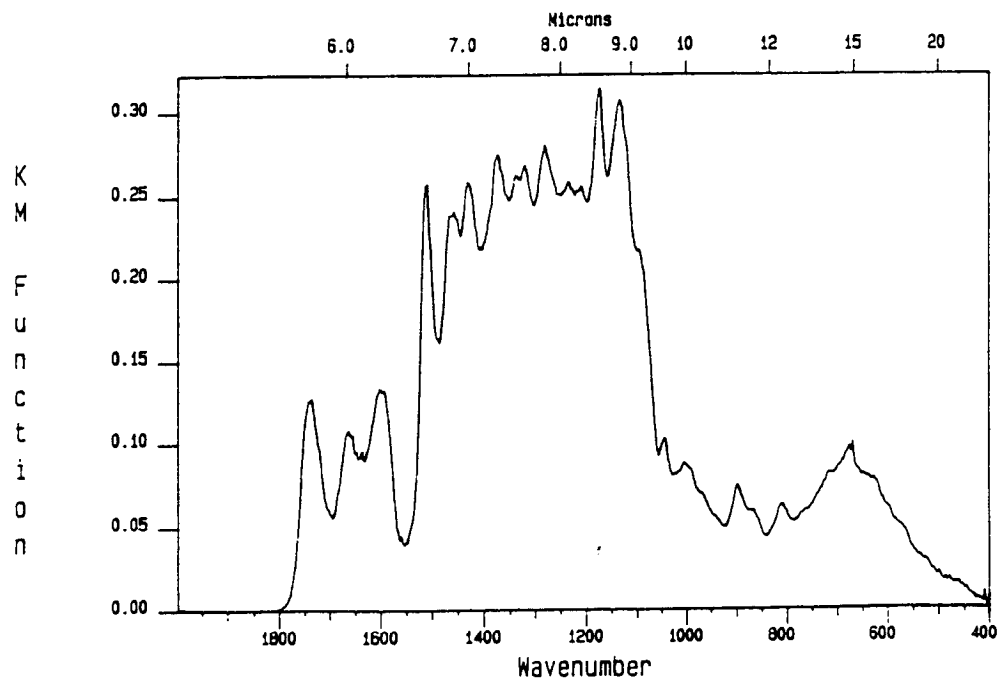


Fig. 1. Infrared spectrum, between 2000 and 400 cm⁻¹, of unweathered Southern pine.

at about 2950 cm^{-1} , and a familiar pattern of characteristic absorption bands between 1800 and 1000 cm^{-1} , some of which are caused by the presence of aromatic groups in the lignin (Fig. 1). In particular, the absorption at 1510 cm^{-1} (aromatic ring breathing mode) is relatively strong, as are the bands at 1664 and 1602 cm^{-1} – both regions characteristic of unsaturated groups. Absorptions at about 1180 and 1140 cm^{-1} , probably attributable to the presence of C-O-H and C-O-C groups, are also strong and well resolved.

Full weathering (light plus water). After 50 h of full weathering, a dramatic decrease in the intensity of the 1510 cm^{-1} peak is observed, together with a concomitant increase in the carbonyl absorption at 1736 cm^{-1} . In addition, the band at 1457 cm^{-1} also decreases in intensity and the 1664 cm^{-1} band loses its definition. The absorptions at 1180 and 1130 cm^{-1} remain strong and well defined, although an absorption at about 1310 cm^{-1} (possibly due to CH_3 groups) decreases in intensity.

After 150 h exposure, the spectral pattern observed is rather similar, except that the 1510 and 1600 cm^{-1} absorptions are a little weaker. Increased exposure to weathering (300 h) results in the virtual disappearance of the aromatic 1510 cm^{-1} absorption and the 1457 cm^{-1} band, together with a decrease in intensity of the 1600 cm^{-1} absorption and a decrease in the relative strength of the carbonyl absorption (Fig. 2). The other fingerprint bands remain somewhat similar to that seen for the control sample, except that the 1320 cm^{-1} peak is smaller. No dramatic changes are observed with increasing weathering in the O-H and C-H bond stretching regions.

Light only. The most significant feature in the spectrum of Southern pine exposed to 50 h of light-only weathering compared with the spectrum of the control is that the carbonyl absorption has increased in intensity by a factor of about two. In addition, the 1510 cm^{-1} aromatic ring absorption has decreased in intensity, and the 1664 cm^{-1} band has changed shape somewhat – moving to higher

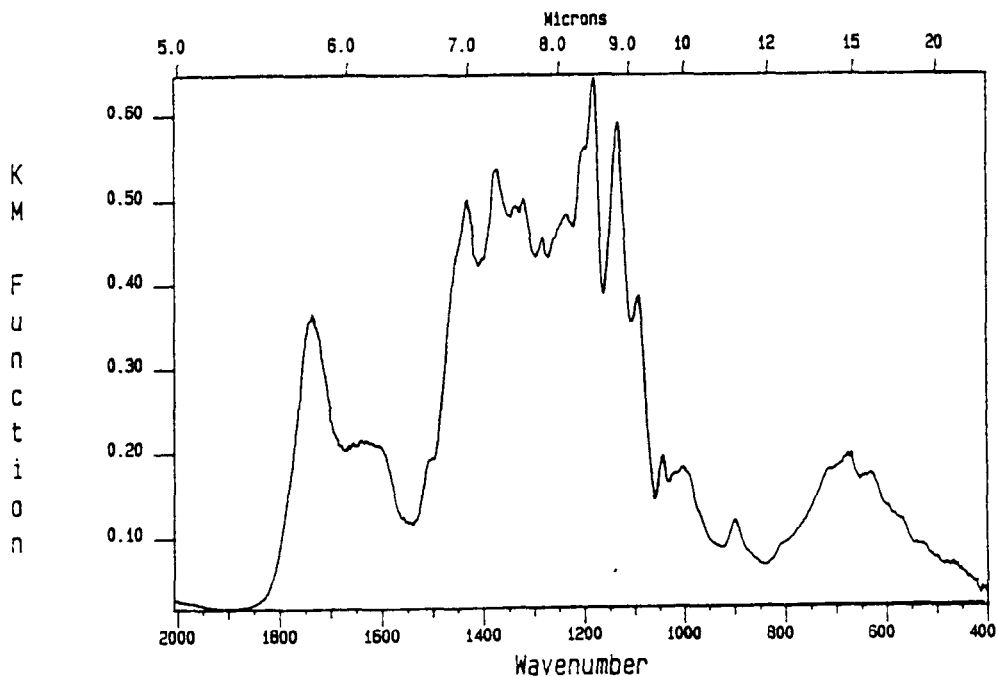


Fig. 2. Infrared spectrum between 2000 and 400 cm^{-1} , of Southern pine weathered with light and water for 300 h.

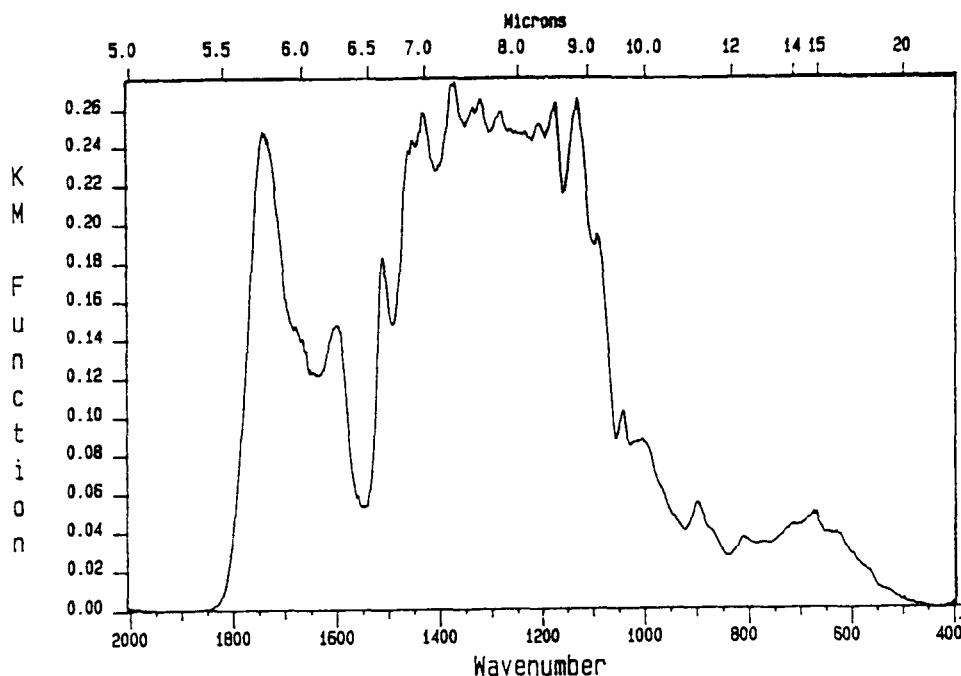


Fig. 3. Infrared spectrum, between 2000 and 400 cm^{-1} , of Southern pine weathered with light only for 300 h.

frequency as a shoulder onto the carbonyl band. These changes are not greatly affected by increased weathering to 300 h, thus strongly implying that the main effect of UV light on wood surfaces occurs quite rapidly (Fig. 3). However, it appears that the definition of the peaks in part of the fingerprint region (1400–1000 cm^{-1}) is reduced slightly by continual exposure to light, and the O-H stretch region centered at about 3400 cm^{-1} becomes much broader.

Water only. The changes observed in the infrared spectra of the surfaces after wood samples were subjected to 50, 150 and 300 h of water-only weathering are minor compared with the effect of light-only and light plus water. No significant differences can be seen in the carbonyl and aromatic bands, however, the effect of water appears to result in a decrease in the intensity of the absorption at about 1200 cm^{-1} . This spectral region in wood has been found to be the most likely to be affected by anomalous intensity effects associated with the DRIFT technique [7], and care

should be exercised in drawing conclusions from intensity changes in this region.

Acetylated wood

A comparison of the spectra of the untreated and acetylated control samples (i.e. unweathered) shows some distinct differences. As might be expected, the acetylated sample has a very intense carbonyl absorption band at 1736 cm^{-1} (Fig. 4). In addition, absorptions at 1378 and 1263 cm^{-1} appear as strong peaks – obviously attributable to the presence of acetyl groups replacing many of the ubiquitous O-H groups in the wood polymer matrix. The strong O-H stretching band is reduced in intensity and width, and the C-H region appears as a fairly strong doublet – again an indication of the presence of new functional groups containing C-H bonds.

Full weathering (light plus water). After 50 h of full weathering, the 1510 and 1460 cm^{-1} bands have decreased in intensity relative to other absorptions. A similar reduction in intensity can be

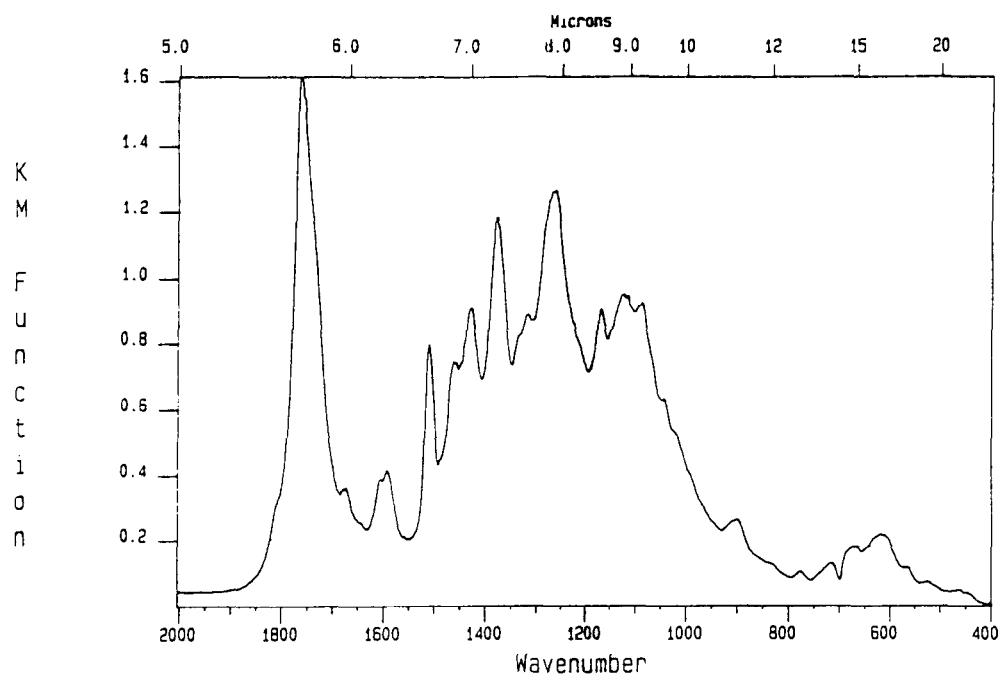


Fig. 4. Infrared spectrum, between 2000 and 400 cm^{-1} , of acetylated Southern pine (unweathered).

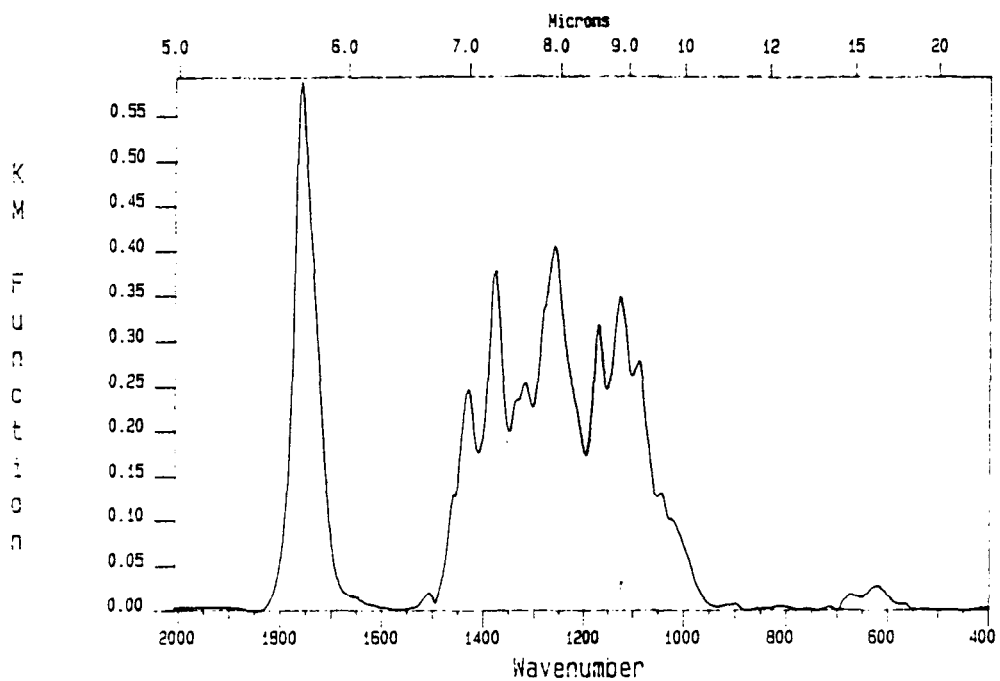


Fig. 5 Infrared spectrum, between 2000 and 400 cm^{-1} , of acetylated Southern pine weathered with light and water for 300 h.

observed for the relatively weak 1600 and 1660 cm^{-1} absorptions. This change is not as pronounced as that seen for untreated wood after a similar exposure period. Further weathering results in an increase in these spectral changes until, after 300 h, the 1510 cm^{-1} peak is reduced to a very small residual bump on the base line (Fig. 5). In addition, all trace of the 1600 and 1660 cm^{-1} absorptions have disappeared. The rest of the fingerprint region is largely unchanged. Any resulting changes in the intensity of the absorptions due to the original carbonyl groups are totally masked by the presence of the intense carbonyl absorptions due to the protecting acetate groups. At the higher wavenumber region, the O-H stretching band remains similar in size and shape, whereas the C-H doublet has become asymmetric – with the higher frequency component decreasing in intensity.

Light only. Exposure to 50 h of UV irradiation causes a slight relative increase in the already intense carbonyl absorption, and a slight decrease

in the aromatic 1510 cm^{-1} peak and in the unsaturated band at about 1600 cm^{-1} . Increased exposure to light merely hastens the diminution of the aromatic bands – although even after 300 h, both the 1510 and the 1460 cm^{-1} absorptions can be clearly observed (Fig. 6). A shoulder to the low frequency edge of the carbonyl absorption (at about 1660 cm^{-1}) intensifies with increased exposure, making the band quite asymmetric. In addition, the width of the O-H stretching band is increased near the base of the envelope – to encompass the C-H absorption.

Water only. No discernible spectral changes can be observed from the action of water on the acetylated wood samples.

Scanning electron microscope data

Untreated wood

The SEM results show clearly that the surface of wood exposed to weathering undergoes distinct physical changes (compare, for example, Figs. 7(a)

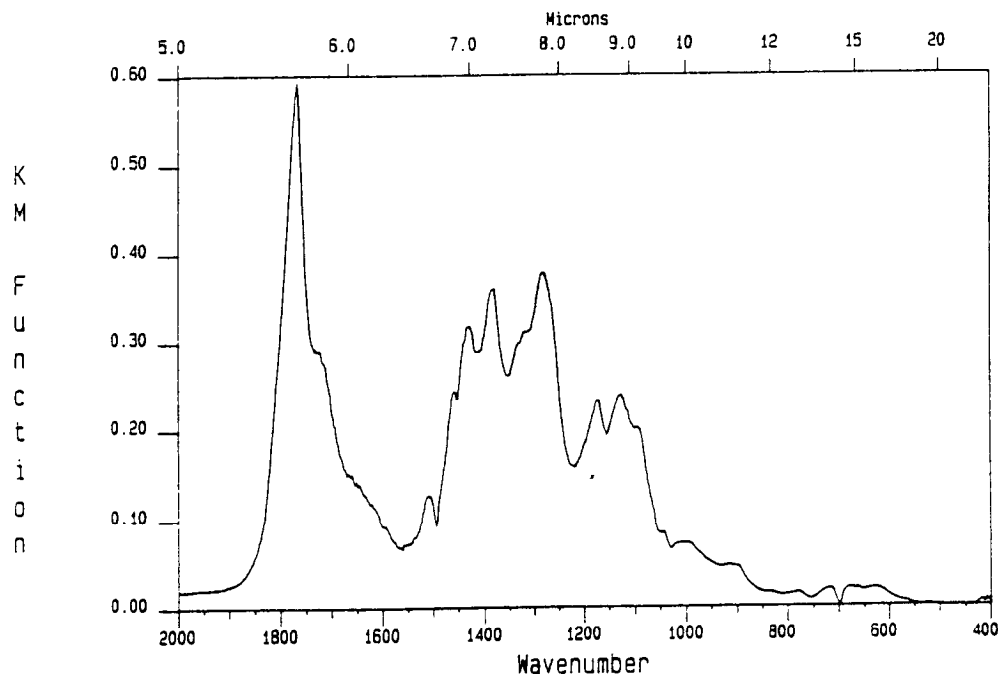


Fig. 6. Infrared spectrum, between 2000 and 400 cm^{-1} , of acetylated Southern pine weathered with light only for 300 h.

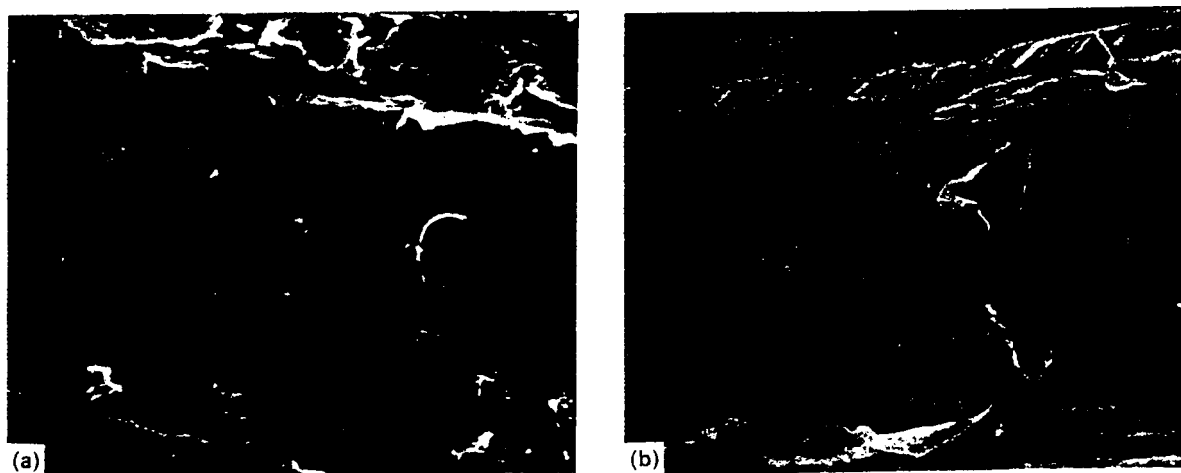


Fig. 7. Scanning electron micrograph ($\times 2000$) of the surface of a radial section of Southern pine: (a) unweathered, (b) weathered with light and water for 300 h.

and 7(b)). The pit structures of the control (unweathered) sample have nearly symmetrically round apertures, and the borders are intact and unblemished. The surface degradation appears to be directly proportional to the time of exposure to the weathering conditions. and after 2400 h of light and water, many of the pit structures coalesce, creating deep crevasses in the wood (Fig. 8(a)). The results show that degradation caused by the full weathering process, comprising both water and UV light, is considerably more rapid and more extensive than exposure to either one parameter

individually. Figure 8(b) illustrates the results of 300 h of exposure to light only. It would appear, from comparison of the pit structures, as though 50 h of full weathering produces approximately the same effect as approximately 300 h of exposure to light only. Our infrared results show that on a molecular level it is difficult to detect significant weathering effects due to the action of water only. However, it is well known that wood exposed to moisture swells easily, and these physical changes are evidenced in the SEM data (Fig. 9(a)). It appears that the pit borders are left largely intact

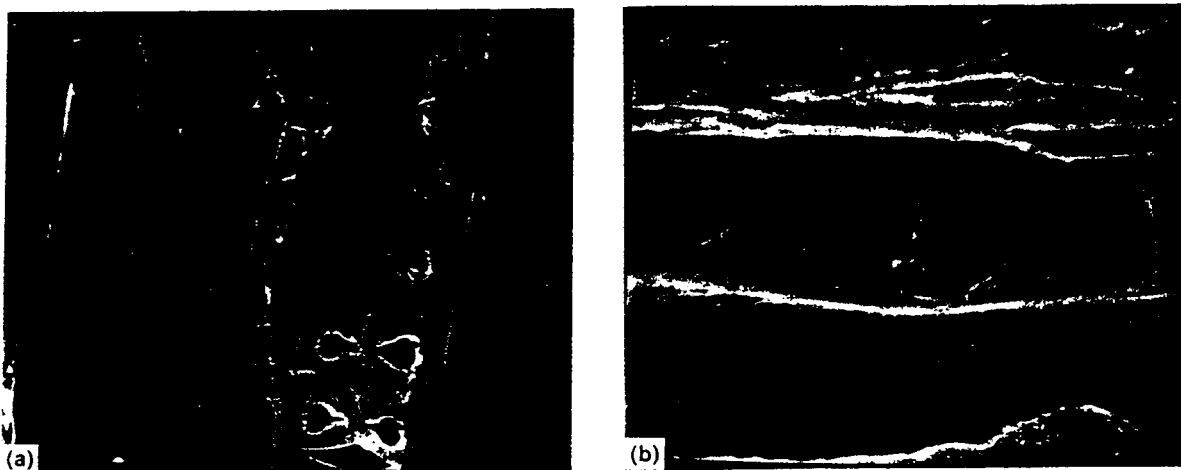


Fig. 8. Scanning electron micrograph of the surface of a radial section of Southern pine: (a) weathered with light and water for 2400 h ($\times 500$). (b) weathered with light only for 300 h ($\times 2000$).



Fig. 9. Scanning electron micrograph of the surface of a radial section of Southern pine: (a) weathered with water only for 300 h ($\times 2000$), (b) acetylated, unweathered ($\times 2000$).

by the effect of water but some structural damage can be observed. That this is not a chemical change is supported by the observation that wood swelling by water is largely reversible with little or no permanent structural damage.

Acetylated wood

The SEM photographs of the weathered acetylated wood generally confirm the infrared results – namely that the extent of weathering is not as pronounced as in the natural wood. This had been reported previously [8]. No discernible

differences can be observed between the SEM photographs of the unweathered normal wood and the unweathered acetylated wood, thus providing some evidence that the chemical treatment did not result in any macroscopic disruption of the normal polymer matrix (Fig. 9(b)). A comparison of all the photographs taken for normal and acetylated wood consistently shows that the extent of weathering (light plus water) for the former is approximately 50% of that for the latter (Figs. 10(a) and 10(b) illustrate this fact). The same conclusion may be drawn from the results of the

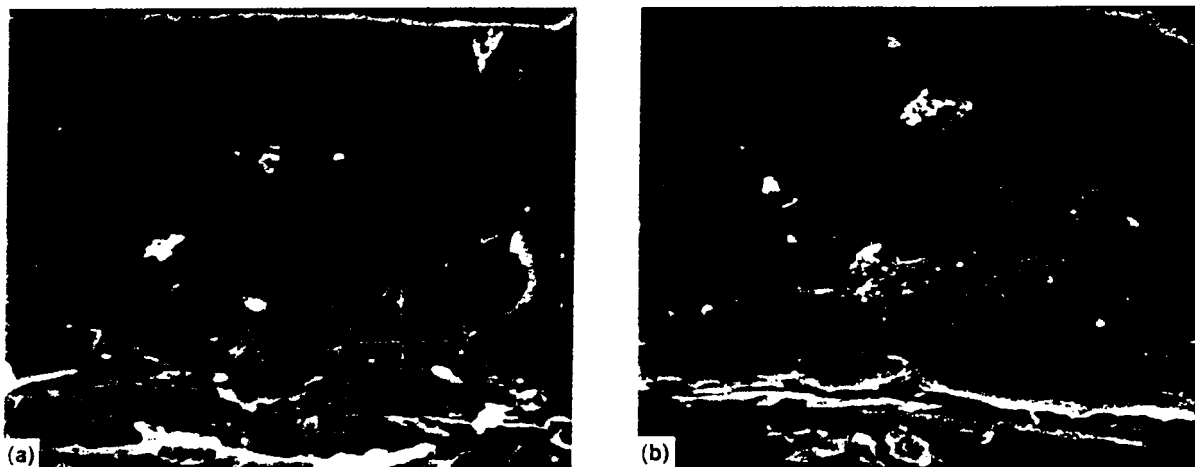


Fig. 10. Scanning electron micrograph of the surface of a radial section of Southern pine: (a) weathered with light and water for 150 h ($\times 2000$), (b) acetylated and weathered with light and water for 300 h ($\times 2000$).

light-only data. For the water-only specimens, the pit boundaries remain unbroken for both normal and acetylated weathered wood and there does not appear to be any recognizable difference between them.

Results and conclusions

Aspects of the phenomenon of weathering in wood have been investigated using several different experimental techniques including optical [2] and infrared [4] methods, scanning electron microscopy [3], ESCA [9], and electron spin resonance spectroscopy [10]. There is general agreement that the process is initiated by UV light, and is primarily a surface phenomenon. The first component of wood to be broken down is lignin [11-13] and some possible photochemical reaction schemes have been proposed for what is obviously quite a complex series of chemical changes [10]. It has also been shown that the rate of degradation of wood exposed to light is approximately 20 times greater in air than in an atmosphere of pure nitrogen, thus the process is a photo-oxidative one [12].

The results of the present study are in good accord with these conclusions, and several other inferences may be drawn from the data.

- (1) The effect of UV light on wood surfaces is quite rapid – noticeable effects are seen after 50 h of light-only artificial weathering, and we have unpublished work showing that the surface changes after 5 h exposure.
- (2) The whole weathering process cannot be represented by one simple chemical reaction. Evidence for this can be seen from the way the carbonyl absorption first of all increases in intensity after light plus water weathering and then decreases.
- (3) Acetylation of wood under mild conditions serves to protect the surface from the weathering effects of light and water. The extent of weathering is reduced by approximately 50%.

In an earlier study, Kalnins investigated the effect of acetylation on the weathering behavior

of wood, and concluded that the degradation was enhanced by the treatment [13]. Kalnins used a different acetylation technique than that used in the present studies. The present results (both SEM and infrared) show quite clearly the opposite effect, and the most likely explanation for this anomaly has to do with the nature of the acetylation treatment. Kalnins' acetylation conditions were quite severe, whereas in the present experiments they were fairly mild. In the former case it seems likely that the treatment might have destroyed the structural integrity of the wood samples even before the weathering treatment.

Although the data obtained from both the SEM and infrared techniques were completely compatible it is useful to note that they represent two quite different pictures of the wood surface. The former detects mainly physical changes whereas the latter monitors the changes in the functional groups of the molecular entities on or near the surface. The acetylation of a wood sample is clearly observed as a dramatic change using infrared spectroscopy, whereas this is not so from the perspective of SEM. The swelling effect of water on wood, however, was detected clearly by SEM but not by infrared spectroscopy.

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