7 Weathering of Wood□

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Weathering is the general term used to define the slow degradation of materials exposed to the weather. The degradation mechanism depends on the type of material, but the cause is a combination of factors found in nature: moisture, sunlight, heat/cold, chemicals, abrasion by windblown materials, and biological agents. Tall mountains weather by the complex and relentless action of these factors. All natural and man-made materials weather; for polymeric materials, the weathering rate is considerably faster than the degradation of mountains. Many of the materials we depend on for clothing and shelter undergo degradation by the weathering process.

Wood is a material that has been used for countless centuries to provide people with shelter. Today we still depend on wood and wood-based products to provide this shelter. Our houses are usually made of wood, and the outermost barrier to the weather is often wood or a wood-based product (siding, windows, decks, roofs, etc.). If these wood products are to achieve a long service life, we must understand the weathering process and develop wood treatments to retard this degradation. Failure to recognize the effects of weathering can lead to catastrophic failure of wood products and other products used with wood. For example, if wood siding is left to weather for as little as one to two weeks before it is painted, the surface of the wood will degrade. During this short exposure period, the surface of the wood will not appear to have changed very much, but damage has occurred. Application of paint after one to two weeks of weathering will not give a durable coating. The surface of the wood has been degraded and it is not possible to form a good paint bond with the degraded surface. The paint will show signs of cracking and peeling within a few years. As the paint peels from the surface, the wood grain pattern can easily be seen on the back side of the paint. The peeling paint has lifted the damaged layer of wood from the sound wood underneath. The reasons for this will become apparent as we discuss the chemistry and degradation processes of wood weathering.

We see many examples of weathering. The rough, gray appearance of old barns, wood shake roofs, and drift wood are typical examples of weathered wood. In the absence of biological attacks, the weathering of wood can give a beautiful bright gray patina.

How does weathering differ from decay? Weathering is surface degradation of wood that is initiated primarily by solar radiation, but other factors are also important. The wetting and drying of wood through precipitation, diurnal and seasonal changes in relative humidity (RH), abrasion by windblown particulates, temperature changes, atmospheric pollution, oxygen, and human activities such as walking on decks, cleaning surfaces with cleaners and brighteners, sanding, and power-washing all contribute to the degradation of wood surfaces. However it is primarily the ultraviolet (UV) portion of the solar spectrum that initiates the process we refer to as weathering. It is a photo-oxidation or photochemical degradation of the surface. The weathering process affects only the surface of the wood. The degradation starts immediately after the wood is exposed to sunlight. First the color changes, then the surface fibers loosen and erode, but the process is rather slow. It can take more than 100 years of weathering to decrease the thickness of a board by 5–6 mm. In addition to the slow erosion process, other processes also occur. The wood may develop checks and a raised grain. Mildew will colonize the surface and discolor the wood. If boards contain compression or juvenile wood, cross-grain cracking may develop. The boards may warp and cup, particularly in decking applications. These other weathering factors such as mildew growth, checking, splitting, and warping, are often more important than the photo-oxidation, but these processes often act in concert to degrade the surface (see Figure 7.1). Note that the figure depicts 100 years
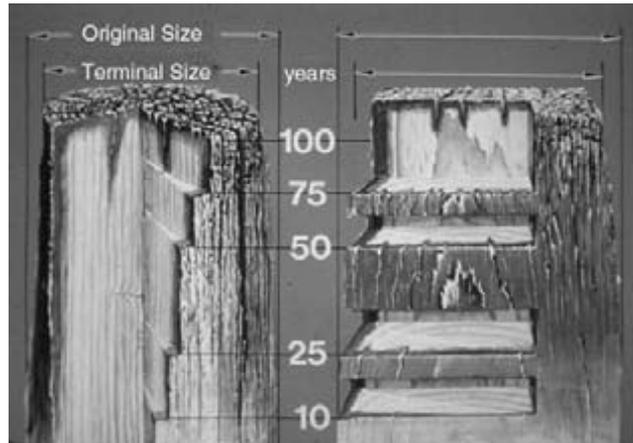
FIGURE 7.1 Simulation of 100 years of weathering of posts showing checking and erosion of the surface.

of weathering, and in addition to the slow loss of wood materials as depicted by the decreased size near the top, the post has also developed severe checking.

On the other hand, wood decay is a process that affects the whole thickness or bulk of the wood. It is caused by decay fungi that infect the wood. *Decay fungi* are plants that grow through the wood cells and release enzymes that break down the wood components that they then metabolize for food. Whereas weathering can take many decades to remove a few millimeters of wood from the surface, decay fungi can completely destroy wood in just a few years if the conditions are favorable for their growth. The critical factor for deterring their growth is to limit the water available to them. Wood cannot decay unless there is free water available in the wood cells. Free water is not necessary for weathering to occur, however the presence of water can help accelerate the process by causing splitting and checking of the wood (see Figure 7.2).

How does weathering differ from light-induced color change? Weathering is caused by the UV radiation portion of sunlight. The UV radiation has sufficient energy to chemically degrade wood structural components (lignin and carbohydrates). The visible portion of sunlight also causes surface changes in wood, but except for minimal damage at the short wavelengths of visible light, the
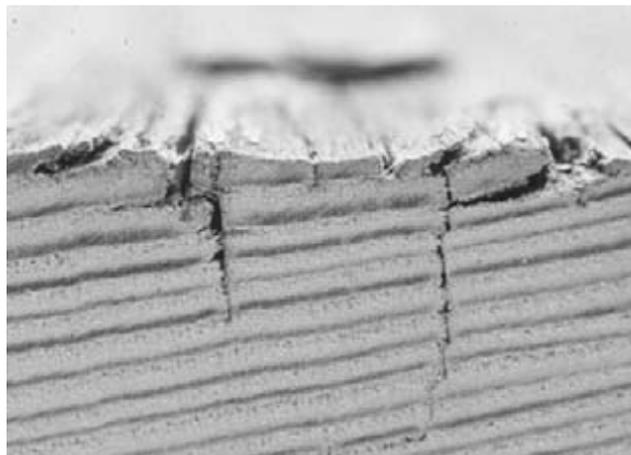

FIGURE 7.2 Cross-section of a board showing checking caused by weathering.

changes do not involve degradation of the wood structure. The chemicals that give wood its color are extractives: organic compounds of various types that may contain halogens, sulfur, and nitrogen. Chemical moieties containing these elements can undergo photo degradation reactions at lower energies than lignin and carbohydrates. So in addition to the UV radiation, visible light has sufficient energy to degrade extractives. They fade much the same as the dyes in textiles. Wood exposed outdoors will undergo a rather rapid color change in addition to the UV-induced degradation of lignin. In addition, rain will leach the water-soluble chemicals from the wood surface. Very little UV radiation can penetrate common window glass; therefore, wood does not undergo UV-catalyzed weathering indoors. The color change that occurs to wood when it is exposed indoors is caused by visible light. The visible light causes the organic dyes in the wood to fade. The color change indoors is not caused by UV light. The use of a UV stabilizer in interior finishes has little effect for achieving color stability. A few recent publications on color change considered pertinent to the mechanism of weathering are included in the chapter.

What is the risk to wood materials if weathering is not understood? Various wood-based products weather in different ways. Some wood products can be allowed to weather naturally to achieve a driftwood gray patina. For example Eastern White Cedar (*Thuja occidentalis*) and Western Red Cedar (*Thuja plicata*) shakes are often left unfinished to weather naturally. However, other wood products, such as plywood, can fail catastrophically within several years if they are not protected from weathering. By understanding the mechanism of weathering—the chemical changes, the effects of degradation on the physical properties, and methods for retarding or inhibiting degradation—it is possible to maximize the service life of all types of wood products in any type of climate.

The purpose of this chapter is to describe the chemical and physical changes that occur to wood during weathering and explore methods for preventing this degradation. Current literature back to 1980 has been reviewed and is included in this chapter. Literature prior to 1980 was reviewed in detail by Feist and Hon (1984) and by Feist (1990).

7.1   BACKGROUND

Understanding the chemistry of UV degradation of wood requires knowledge of its macroscopic properties, anatomical structure, chemical nature of polysaccharides, lignin, and extractives, the UV spectrum, and the interactions of UV radiation with various chemical moieties in wood.

7.1.1   Macroscopic Properties

Wood is a natural biological material and as such, its properties vary not only from one species to another but also within the same species. Some differences can even be expected in boards cut from the same tree. Within a species, factors that affect the natural properties of wood are usually related to growth rate. Growth rate in turn is determined by climatic factors, geographic origin, genetics, tree vigor, and competition—factors over which we currently have little control. In addition to the natural properties, manufacturing influences the surface properties of wood: the grain angle, surface roughness, and amount of earlywood/latewood and heartwood/sapwood.

7.1.1.1   Specific Gravity

The properties of wood that vary greatly from species to species are specific gravity (density), grain characteristics (presence of earlywood and latewood), texture (hardwood or softwood), presence of compression wood, presence and amount of heartwood or sapwood, and the presence of extractives, resins, and oils. The specific gravity of wood is one of the most important factors that affect weathering characteristics. Specific gravity varies tremendously from species to species (see Table 7.1) and it is important because "heavy" woods shrink and swell more than do "light" woods. This dimensional change in lumber and, to a lesser extent, in reconstituted wood products and

TABLE 7.1
Characteristics of Selected Woods for Painting

Wood Species	Specific Gravity[a] Green/Dry	Shrinkage (%)[b]	
		Flat Grain	Vertical Grain
Softwoods			
Bald cypress	0.42/0.46	6.2	3.8
Cedars			
Incense	0.35/0.37	5.2	3.3
Northern white	0.29/0.31	4.9	2.2
Port-Orford	0.39/0.43	6.9	4.6
Western red	0.31/0.32	5	2.4
Yellow	0.42/0.44	6	2.8
Douglas-fir[c]	0.45/0.48[d]	7.6	4.8
Larch, western	0.48/0.52	9.1	4.5
Pine			
Eastern white	0.34/0.35	6.1	2.1
Ponderosa	0.38/0.42	6.2	3.9
Southern	0.47/0.51[e]	8	5
Sugar	0.34/0.36	5.6	2.9
Western white	0.36/0.38	7.4	4.1
Redwood, old growth	0.38/0.40	4.4	2.6
Spruce, Engelmann	0.33/0.35	7.1	3.8
Tamarack	0.49/0.53	7.4	3.7
White fir	0.37/0.39	7.0	3.3
Western hemlock	0.42/0.45	7.8	4.2
Hardwoods			
Alder	0.37/0.41	7.3	4.4
Ash, white	0.55/0.60	8	5
Aspen, bigtooth	0.36/0.39	7	3.5
Basswood	0.32/0.37	9.3	6.6
Beech	0.56/0.64	11.9	5.5
Birch, yellow	0.55/0.62	9.5	7.3
Butternut	0.36/0.38	6.4	3.4
Cherry	0.47/0.50	7.1	3.7
Chestnut	0.40/0.43	6.7	3.4
Cottonwood, eastern	0.37/0.40	9.2	3.9
Elm, American	0.46/0.50	9.5	4.2
Hickory, shagbark	0.64/0.72	11	7
Magnolia, southern	0.46/0.50	6.6	5.4
Maple, sugar	0.56/0.63	9.9	4.8
Oak			
White	0.60/0.68	8.8	4.4
Northern red	0.56/0.63	8.6	4.0
Sweetgum	0.46/0.52	10.2	5.3
Sycamore	0.46/0.49	8.4	5
Walnut	0.51/0.55	7.8	5.5
Yellow-poplar	0.40/0.42	8.2	4.6

[a] Specific gravity based on weight ovendry and volume at green or 12% moisture content.
[b] Value obtained by drying from green to ovendry.
[c] Lumber and plywood.
[d] Coastal Douglas-fir.
[e] Loblolly, shortleaf, specific gravity of 0.54/0.59 for longleaf and slash.

plywood occurs as wood, particularly in exterior applications, gains or loses moisture with changes in the relative humidity and from periodic wetting caused by rain and dew. Excessive dimensional change in wood stresses the surface to cause checking.

The amount of warping and checking that occurs as wood changes dimensions and during the natural weathering process is also directly related to wood density. Cupping is probably the most common form of warp. *Cupping* is the distortion of a board that causes a deviation from flatness across the width of the piece. Wide boards cup more than do narrow boards. Boards may also twist or warp from one end to the other, deviating from a straight line along the length of the piece. Warping is generally caused by uneven shrinking or swelling within the board. Furthermore, checks, or small ruptures along the grain of the piece may develop from stress set up during the drying process or from stresses caused by the alternate shrinking and swelling that occurs during service. High-density (heavy) woods such as southern yellow pine tend to warp and check more than do the low-density (light) woods such as redwood.

7.1.1.2 Earlywood and Latewood

The presence and amount of latewood in softwood (conifer) lumber is closely related to wood density (see Figures 7.3a and 7.3b). Each year, tree species growing in temperate climates add one
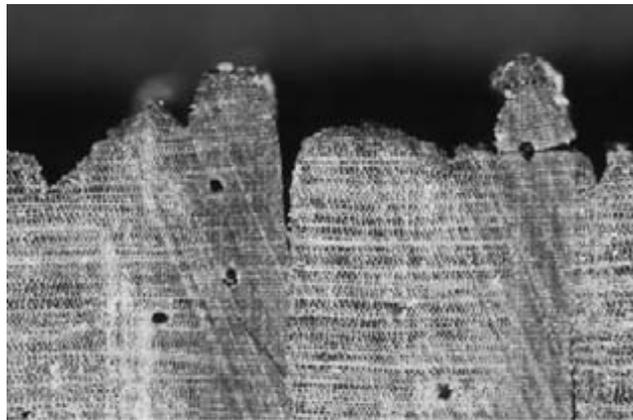
(a)
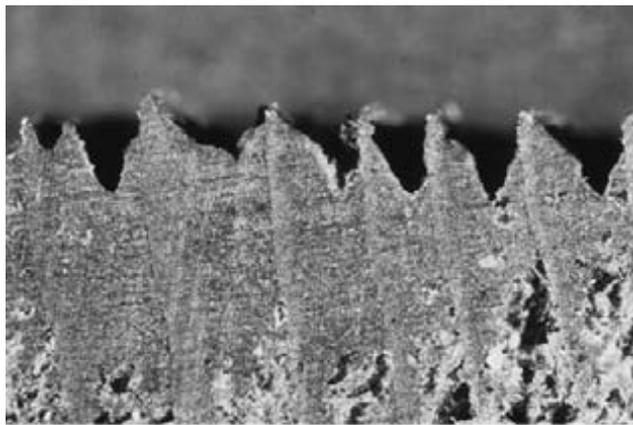
(b)

FIGURE 7.3 Micrographs of cross-sections of weathered boards showing earlywood and latewood bands (3X): a) southern pine; b) western redcedar.
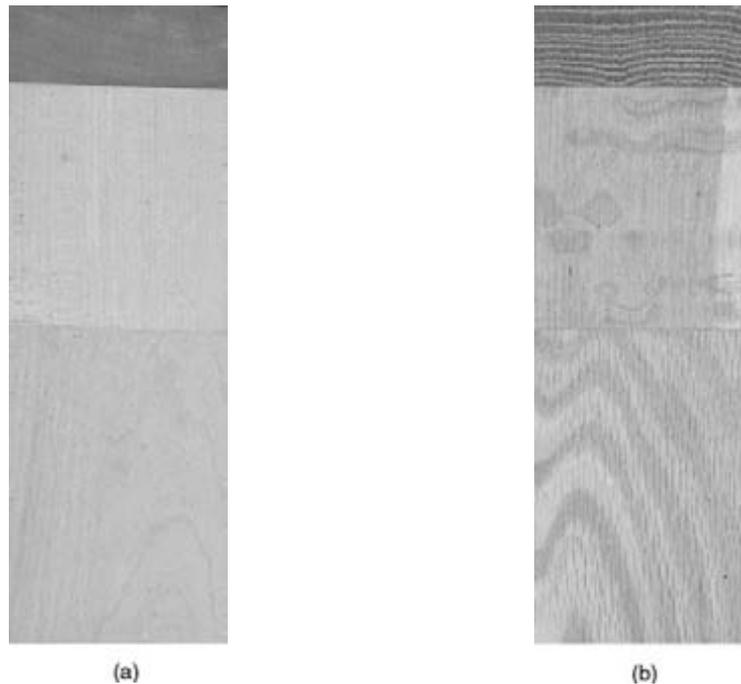
FIGURE 7.4 Surface texture of diffuse porous sugar maple (a) and ring porous red oak (b): top, end grain; middle, radial grain; bottom, tangential grain.

growth increment or ring to their diameter. For most species, this ring shows two distinct periods of growth and therefore two bands, called earlywood (springwood) and latewood (summerwood). Latewood is denser, harder, smoother, and darker than earlywood, and its cells have thicker walls and smaller cavities. The wider the latewood band, the denser the wood. Wide latewood bands are normally absent from edge-grained cedar and redwood, however, they are prominent in southern yellow pine and Douglas-fir, two of the most common species used for general construction and for the production of plywood.

7.1.1.3 Texture

Texture refers to the general coarseness of the individual wood cells and is often used in reference to hardwoods (see Figures 7.4a and 7.4b). Figure 7.4a shows fine-textured diffuse-porous sugar maple (*Acer saccharum*) and Figure 7.4b shows coarse-grained ring-porous red oak (*Quercus rubra*). Hardwoods are primarily composed of relatively short, small-diameter cells (fibers) and large-diameter pores (vessels); softwoods, in contrast, are composed of longer small-diameter cells (tracheids). The size and arrangement of the pores may outweigh the effect of density and grain pattern on weathering. Hardwoods with large pores, such as oak and ash, may erode more quickly at the pores than the surrounding fibers.

7.1.1.4 Juvenile Wood

Juvenile wood forms during the first eight to ten years of a tree's growth. It differs form normal wood in that the fibrils in the wood cell wall are oriented more across the width of the cell rather than along its length. This change in orientation gives juvenile wood a rather large longitudinal dimensional change as it changes moisture content. Whereas normal wood shrinks only about 0.1–0.2% as it changes moisture content from green to oven dry, juvenile wood and compression

FIGURE 7.5   Cross-grain checking in juvenile wood.

wood can shrink as much as 2% (*Wood Handbook* 1999). This can cause serious warping and cross-grain cracking as wood weathers (see Figure 7.5).

7.1.1.5 Compression Wood

Compression wood is formed on the lower side of leaning softwood trees. The part of the growth ring with compression wood is usually wider than the rest of the ring and has a high proportion of latewood. As a result, the tree develops an eccentrically-shaped stem and the pith is not centered. Compression wood, especially the latewood, is usually duller and more lifeless in appearance than the rest of the wood. Compression wood presents serious problems in wood manufacturing because it is much lower in strength than is normal wood of the same density. Also, it tends to shrink excessively in the longitudinal direction, which causes cross-grain checking during weathering.

7.1.1.6 Heartwood and Sapwood

As trees mature, most species naturally develop a darker central column of wood called heartwood. The darker color is caused by the deposition of colored extractives. To the outside of the heartwood is a lighter cylinder of wood called sapwood. The sapwood is composed of live cells that serve to transport water and nutrients from the roots to the leaves and to provide mechanical support for the tree. The heartwood, on the other hand, serves only as support. Heartwood is formed as the individual cells die and are impregnated with extractives, pitch, oil, and other extraneous materials. Older trees have a higher percentage of heartwood as compared to younger trees. Some species such as southern yellow pine have a much wider sapwood zone than do species like the cedars and redwood. During the early stage of weathering, it is the heartwood that quickly loses its color because of leaching of the extractives. Other than the presence of extractives, the anatomy (and therefore the components) of cellulose, hemicellulose, and lignin are the same for heartwood and sapwood.

7.1.2 ANATOMICAL STRUCTURE OF WOOD

Typical anatomical structure for softwoods and hardwoods show distinct differences. Hardwoods contain specialized cells (pores or vessels) for liquid transport and these can occur more or less evenly spaced (diffuse porous; see Figure 7.6a) or bunched near the early wood in some temperate hardwoods (ring porous; see Figure 7.6b) as shown for Yellow Poplar (*Liriodendron tulipifera* L.) and White Oak (*Quercus alba* L.). Water transport in softwoods takes place via the tracheids and flows from one tracheid to another through bordered pits (holes in the side of the tracheid).
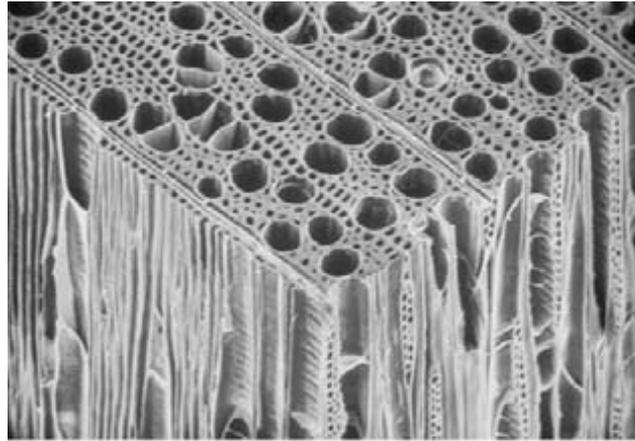
(a)
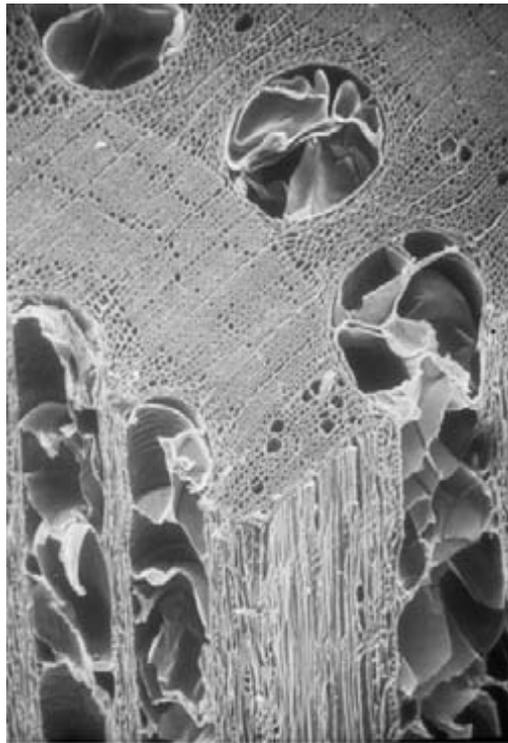
(b)

FIGURE 7.6 Micrographs of hardwoods: a) diffuse-porous; b) ring-porous.

As discussed earlier in Chapter 2, wood contains other types of specialized cells; however, these cells do not have any special effect on weathering.

An expanded view of a typical tracheid shows the primary wall and S_1, S_2, and S_3 layers (see Figure 3.12, Chapter 3). A micrograph of a typical softwood cross-section is also shown for comparison (see Figure 7.7). Note that the fibril angle with respect to the length of the tracheid is almost uniaxial. The area between wood cells is the *middle lamella* and the center hollow area is the *lumen*. When viewed in cross-section, the largest component of the cell wall is the S_2 layer.
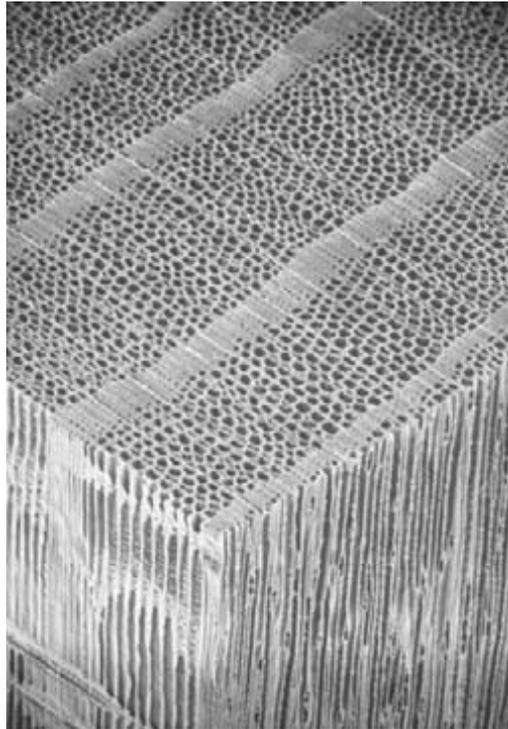
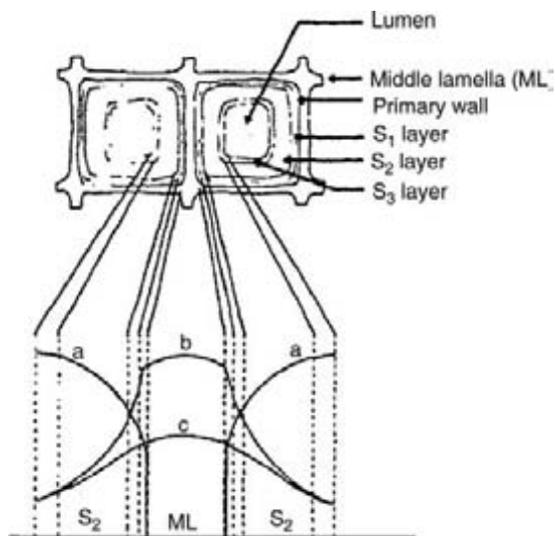**FIGURE 7.7**   Micrograph of a softwood.

FIGURE 7.8 Diagram showing the relative amounts of cellulose, hemicellulose, and lignin across a cross-section of two wood cells: a) cellulose; b) lignin; c) hemicellulose.
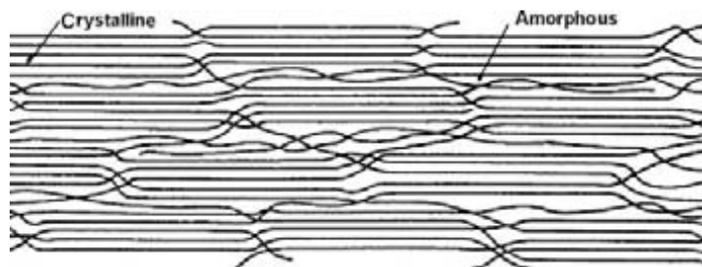
FIGURE 7.9 Diagram showing amorphous and crystalline regions of cellulose.

The components of the various layers differ in the chemical constituents and in the orientation of the fibrils within each layer. The fibril orientation can also differ for juvenile wood (see Section 1.1.4 of this chapter on juvenile wood). The fibril orientation and the chemical constituents greatly affect the way in which wood weathers. Figure 3.12 in Chapter 3 shows the relative ratios of the three main polymeric constituents of the cell wall. The concentration of cellulose is highest in the S_2 layer, whereas the lignin concentration is highest in the middle lamella (see Figure 7.8).

7.1.3 CHEMICAL NATURE OF POLYSACCHARIDES, LIGNIN, AND EXTRACTIVES

Approximately 2/3 of the mass of wood is comprised of sugars. (Kollmann and Côté 1968) Cellulose is a linear polymer of (β-1→4)-D-glucopyranose and occurs primarily in the S_2 layer of the cell wall. It can be crystalline or amorphous, and a single cellulose chain may run through several alternating amorphous and crystalline regions (see Figure 7.9). Wood cellulose is about 60–70% crystalline. The glucopyranose forms high molecular-weight polymers through the 1→4 glycocidic bond to form straight chains having all three hydroxyls in the equatorial plane (see Figure 3.2, Chapter 3). It is the alternating β-linkage and the equatorial hydroxyls that permit cellulose to form crystalline regions. Hemicelluloses do not have this property. They are rather small macromolecules of approximately 150–200 sugar units (primarily L-arabinose, D-galactose D-glucose, D-mannose, D-xylose and 4-O-methyl-D-glucuronic acid). The polymers are essentially linear with numerous short side chains. The hemicelluloses in hardwoods and softwoods are quite different: hardwoods contain primarily glucurono-xylan and glucomannan, whereas softwoods contain arabinoxylzn and galactoglucomannan. The composition of the various polysaccharide in hardwoods and softwoods is shown in Table 7.2. The polysaccharides are comprised of simple sugars and they contain no conjugated systems or carbonyl groups.

Lignin is a three-dimensional polymer comprised of phenyl propane units, but it has no regular structure. Lignin cannot be isolated from wood without degrading it, so it has not been possible to determine its molecular weight. Estimates range as high as 50 million Daltons. One of the common representations for softwood lignin shows a structure with multiple conjugated systems and carbonyl groups (see Figure 3.10, Chapter 3). It should be emphasized that this is not a structure but merely a representation of typical groups in softwood lignin. The basic unit is a phenyl propane (see Figure 7.10a), and in softwoods, there is usually an oxygen and methoxy group giving a methoxy-phenyl propane (guaiacyl propane, see Figure 7.10b). Hardwoods have an additional methoxy group (see Figure 7.10c). In addition, there are approximately 20 carbonyls per each 100 guaiacyl propane. For additional information on lignin structure, refer to Kollmann and Côté (1968).

7.1.4 UV SPECTRUM

The UV and visible solar radiation that reaches the earth's surface is limited to the range between 295–800 nm. Wavelengths from 800 to about 3000 are infrared radiation. The radiation from 295–3000 nm comprises distinct ranges that affect weathering: UV radiation, visible

TABLE 7.2
Cellulose and Hemicellulose Composition
of Hardwoods and Softwoods[a]

Polysaccharide	Occurrence	Percent of Extractive-Free Wood
Cellulose	All woods	42 ± 2
O-Acetyl-4-O-methyl-glucuronoxylan	Hardwoods	20–35
Glucomannan	Hardwoods	3–5
Arabino-4-O-methyl-glucuronoxylan	Softwoods	10–5
Galactoglucomannan (Water-soluble)	Softwoods	5–10
Galactoglucomannan (Alkali-soluble)	Softwoods	10–15
Arabinogalactan	Larch wood	10–20

[a]Abstracted from Table 2.6, Kollmann and Côté, 1968.

light, and infrared radiation (IR) (see Table 7.3). The energy from the sun that reaches the earth's surface as discrete bundles of energy called *photons* and their energy can be calculated from:

$$E = h = hc/\lambda \tag{7.1}$$

where
  h = Planck's constant
  v = frequency
  c = velocity of radiation
  λ = wavelength of radiation.

From this equation, the photon energy is inversely proportional to the wavelength of the radiation (see Figure 7.11). The energy of the photon will become important when we consider the photochemical reactions that this radiation can initiate.
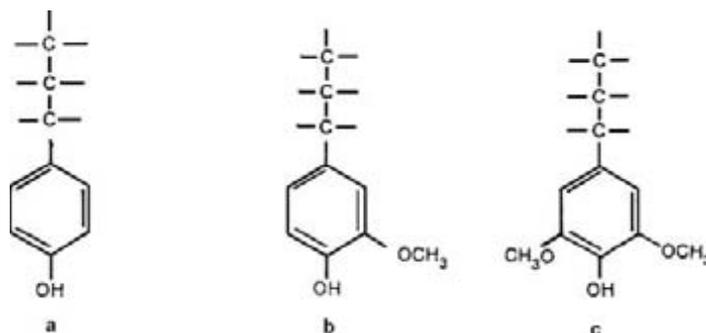

FIGURE 7.10 Units of lignin.

TABLE 7.3
Percent of Total Spectral Irradiance for UV, Visible, and IR Radiation

Radiation	Wavelength Range	% of Total Irradiance
UV radiation	295-400 nm	6.8
Visible light	400-800 nm	55.4
Infrared radiation	800-3000 nm	37.8

Several terms need to be defined before continuing the discussion of solar energy:

Irradiance—the radiant flux per surface area (Watts/m^2 (W/m^2))
Spectral irradiance—irradiance measured at a wavelength (W/m^2/nm)
Radiant exposure—irradiance integrated over time (Joules/m^2 (J/m^2))
Spectral radiant exposure—radiant exposure measured at a wavelength (J/m^2/nm).

When using the irradiance term, it is necessary to define the spectral range (for example, the total solar irradiance (295–3000 nm) or the total UV irradiance (295–400 nm)). For exposure or measurement at a particular wavelength (such as 340 nm), the spectral irradiance would be expressed as W/m^2 at 340nm. The radiant exposure and spectral radiant exposure are irradiance and spectral irradiance integrated over time.

By plotting the spectral irradiance (W/m^2/nm) as a function of wavelength, one gets the spectral power distribution (see Figure 7.12). The plot gives the spectral irradiance at each wavelength. By integrating the areas under the curve for UV radiation (295–400 nm), visible light (400–800 nm), and IR radiation (not shown in the figure), the percent of total irradiance for each component can be calculated.

As seen in Figure 7.12 and Table 7.3, the energy in the UV portion of the spectral power distribution is quite low compared to the total energy in the spectral power distribution. This means that although the energy for photons at 300 nm is quite high, there aren't very many of them, so the spectral irradiance is quite low. As the wavelength increases to 400 nm, the spectral irradiance increases (lower energy photons, but more of them).

7.1.5 WAVELENGTH INTERACTIONS WITH VARIOUS CHEMICAL MOIETIES

In order for a photochemical reaction to occur, sufficient energy to disrupt a chemical bond (bond dissociation energy) must be absorbed by some chemical moiety in the system. The bond
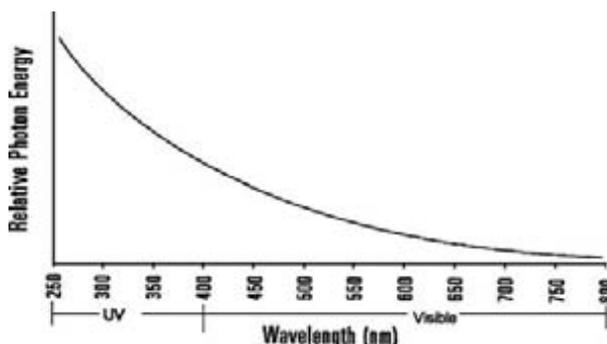

FIGURE 7.11 Relative photon energy versus wavelength for UV radiation and visible light.
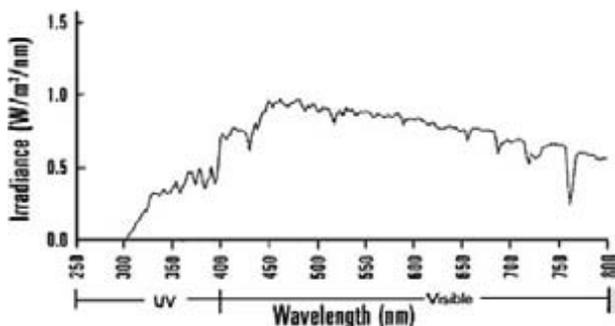
FIGURE 7.12 Spectral power distribution for UV radiation and visible light at the Earth's surface.

dissociation energy available for radiation in the UV and visible range is given in Figure 7.13. The absorbed energy may not result in a degrading chemical reaction, but the absorption is a necessary condition. The bond dissociation energies and corresponding wavelengths having the necessary energy for breaking these bonds for several chemical moieties are listed in Table 7.4. Using Equation 7.1, the energy for UV radiation at a wavelength of 295 nm is about 97 Kcal/mole and for 400 nm is about 72 Kcal/mole. Several of the chemical moieties have bond dissociation energies well above the energy of terrestrial UV radiation and therefore cannot be affected by natural UV radiation. The bond dissociation energy must be below 97 kcal/mole for the chemical moiety to absorb radiation. It can be seen from this table that the bond dissociation energies for many of carbon-oxygen moieties commonly found in lignin fall within the UV radiation range (295–400 nm).

7.2 CHEMICAL CHANGES

There have been many studies to investigate the mechanism of wood weathering, and it has been clearly shown that the absorption of a UV photon can result in the formation of a free radical, and that through the action of oxygen and water, a hydroperoxide is formed. Both the free radical and hydroperoxide can initiate a series of chain scission reactions to degrade the polymeric components of wood. Despite many studies spanning several decades, the mechanism is still not well defined and can only be represented in a general way (see Figure 7.14). The absorption of a photon can
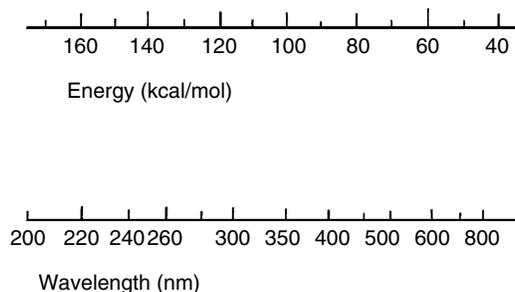

FIGURE 7.13 Bond-dissociation energy compared with wavelength of UV and visible solar radiation.

TABLE 7.4
Bond Dissociation Energies and Radiation Wavelength[a]

Bond	Bond Dissociation Energy (Kcal/mol)	Wavelength (nm)
C–C (Aromatic)	124	231
C–H (Aromatic)	103	278
C–H (Methane)	102	280
O–H (Methanol)	100	286
C–O (Ethanol)	92	311
C–O (Methanol)	89	321
CH_3COO–C (Methyl ester)	86	333
C–C (Ethane)	84	340
C–Cl (Methyl chloride)	82	349
C–$COCH_3$ (Acetone)	79	362
C–O (Methyl ether)	76	376
CH_3–SH (Thiol)	73	391
C–Br (Methyl bromide)	67	427
N–N (Hydrazine)	57	502
C–I (Methyl iodide)	53	540

[a] Bond energies abstracted from Table 2.1 (Rånby, B. and J.F. Rabek 1975).

cause the formation of a free radical that initiates a number of reaction pathways. Many unanswered questions remain:

Is there a wavelength dependence on the rate of the degradation?☐
If there is wavelength dependence, what functional moieties are affected?☐
How do studies using UV radiation <290 nm relate to the actual UV spectrum? ☐
What is the rate-limiting step in this series of reactions?☐
Does the degradation follow the "law of reciprocity"?☐
Once the free radical is formed, is there a rate-limiting chemical?☐
Does the diffusion rate of oxygen affect the reaction?☐
Is water necessary for the reaction?☐
Is hydrolysis of hemicellulose an important component of weathering?☐
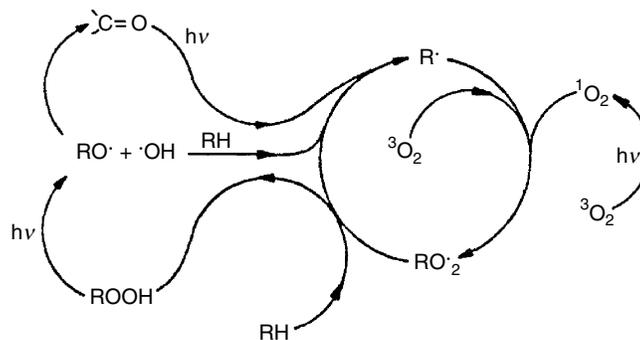What is the temperature dependence?☐

FIGURE 7.14 Mechanism of photodegradation of wood (Feist and Hon 1984).

As was previously discussed, UV radiation comprises only a small part of the total irradiance (spectral power distribution) that strikes the Earth's surface; however, the energy per photon is higher for UV radiation. The energy per photon increases as the wavelength decreases. The energy required to break chemical bonds depends on the type of chemical bond (see Table 7.4). The photon energy per wavelength is shown in Figure 7.13. By comparing the energy available from the photons in the UV range of the spectrum, it is apparent that there is sufficient energy to break bonds in the chemicals that comprise wood. However, in order for a bond to break, energy must be absorbed by some component of the wood. This is the first law of photochemistry (the Grotthus-Draper Principle). In addition, a particular molecule in the wood can absorb only one quantum of radiation (the Stark-Einstein Principle) (McKellar and Allen 1979). The absorbed energy puts the molecule in a higher energy (excited) state that can be dissipated through a number of paths. The most benign would be a return to the ground state through dissipation of heat. Other alternatives would involve chemical reactions.

7.2.1 Free Radical Formation

In early work by Kalnins (1966), he proposed a free-radical initiation and the necessity of oxygen. He isolated volatile degradation products, noted the decrease in lignin content, characterized the IR spectrum of the wood surface following irradiation, noted the post-irradiation reactions, evaluated the effect of extractives, and analyzed surface and interior cellulose and lignin contents of nine wood species. His work established a basis for subsequent studies by others. The results showed in a qualitative way many of the important aspects of weathering, but the light sources did not represent the UV light at the Earth's surface. About 85% of the energy of the lamp was at wavelengths below 295 nm.

Studies to elucidate free-radical formation in wood by the absorption of photons were done by Hon and his collaborators and are covered in detail in Chapter 8 of *Developments in Polymer Degradation—3* and references therein (Hon 1981a). Through a series of experiments, it was clearly shown that the absorption of a photon by wood results in formation of free radicals. In all of these early studies, the light source had UV wavelengths down to 254nm. The energy at this wavelength is approximately 135 Kcal/mole, about 30 kcal/mole higher than the most energetic photons found at the Earth's surface (see Figure 7.13). It is difficult to relate these higher energies to the exact chemical moiety important in the degradation; however, the work clearly showed the importance of free radicals in the degradation process.

One of the common chemical reaction paths following the absorption of a quantum of energy is chemical dissociation to form a free radical. Since wood does not normally have free radicals, their presence following UV irradiation signals the dissociation of a chemical bond (Hon et al. 1980, Hon 1981a, Zhao et al. 1995). These free radicals can easily be detected using electron spin resonance (ESR). A simple ESR spectrum of wood irradiated with UV radiation of different intensities is shown in Figure 7.15. The ESR signal intensity for various exposure times and storage at ambient conditions for different UV radiation sources showed a dependence on the radiation intensity (Figure 7.16). In simple radicals such as a methyl radical, the spin of the free electron interacts with the hydrogen to produce splitting. This splitting can be used to infer the chemical structure. More information on the technique can be found in many texts on photo degradation, such as *Photodegradation, Photo-oxidation and Photostabilization of Polymers* by Rånby and Rabek (1975).

In studies of wood surfaces and model compounds using UV radiation >254nm, Hon showed that the formation and decay rate of free radicals was temperature dependent (Hon 1981a). Interpretation of ESR spectra of lignin was not possible because the splitting patterns were extremely complex. The reactive moieties in lignin include various carbonyls, carboxyls, and ethers, and the ESR signal may be comprised of several types of free radicals. Several model compounds were studied (Figure 7.17) and it was found that compounds a, b, and c were cleaved at the carbon-carbon bond adjacent to the -carbonyl via a Norrish Type I reaction. The ESR spectrum for
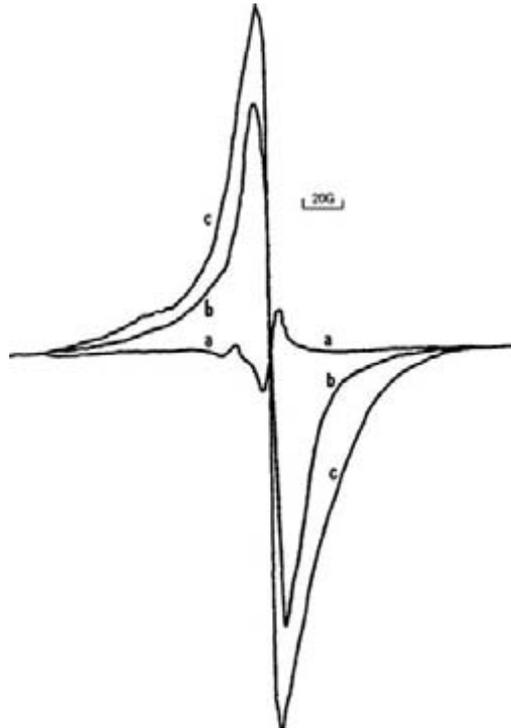
FIGURE 7.15 Electron spin resonance (ESR) signals from wood irradiated with different radiation sources (77°K for 60 min): a) fluorescent light; b) sunlight; c) UV radiation (Feist and Hon 1984).

compound-a showed a seven-line signal for an ethyl radical superimposed on a singlet for an acyl radical. Other compounds decomposed to form phenoxy radicals (see Figure 7.18). From the work on these model compounds, Hon concluded the following (Hon 1981a).

- • "Phenoxy radicals are readily produced from phenolic hydroxy groups by the action of light.
- • Carbon-carbon bonds adjacent to α-carbonyl groups are photo-disassociated via the Norrish Type I reaction.
- • The Norrish Type I reaction does not occur efficiently in those compounds with ether bonds adjacent to the α-carbonyl Group. Photo-dissociation takes place at the ether bond.

FIGURE 7.16 Electron spin resonance (ESR) signals from wood irradiated for a period of time then stored without radiation: 1) vacuum/control; 2) vacuum/fluorescent lamp; 3) air/control; 4) air/fluorescent lamp; 5) vacuum/sunlight; 6) air/sunlight (Feist and Hon 1984).

a $R_1 = CH_3$, $R_2 = H$ d $R = CH_3$
b $R_1 = C_6H_5CH_2$, $R_2 = H$ e $R = C_6H_5CH_2$
c $R_1 = CH_3$, $R_2 = Br$
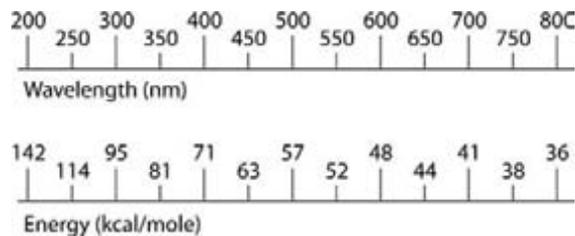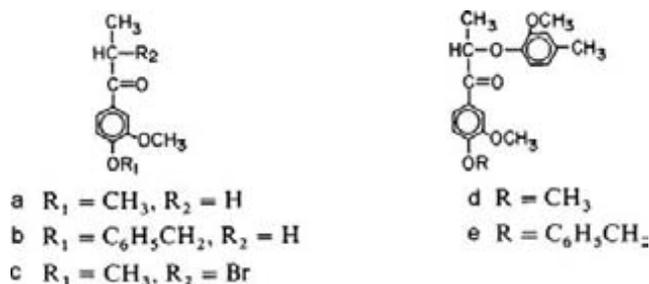
FIGURE 7.17 Lignin model compounds (Hon 1981).

- • Compounds bearing benzoyl alcohol groups are not susceptible to photo-dissociation except when photosensitizers are present.
- • α-Carbonyl groups function as photosensitizers in the photo-degradation."

On the basis of the work with these model compounds, Hon concluded that the phenoxy radicals were the major intermediate formed in the photo degradation of lignin, and that these intermediates react with oxygen and demethylate to form an *o*-quinonoid structure (see Figure 7.19). In recent work by Kamoun et al. (1999) using ESR to evaluate photo degradation of lignin extracts from radiata pine, the formation of a phenoxy radical was confirmed. They proposed that the phenoxy radical is resonance stabilized by radical transfer reactions and confers stabilization to wood.

Two of the most interesting reports from early studies of lignin degradation involved measuring the yellowing of lignin model compounds (Lin and Kringstad 1970, Lin 1982). Twenty-seven

FIGURE 7.18 Electron spin resonance (ESR) spectrum of model compound d: solid line, signal following UV irradiation at 254 nm (77°K for 60 min); dotted line, signal after the irradiated specimen warmed to 298°K.

FIGURE 7.19 O-quinonoid moiety.

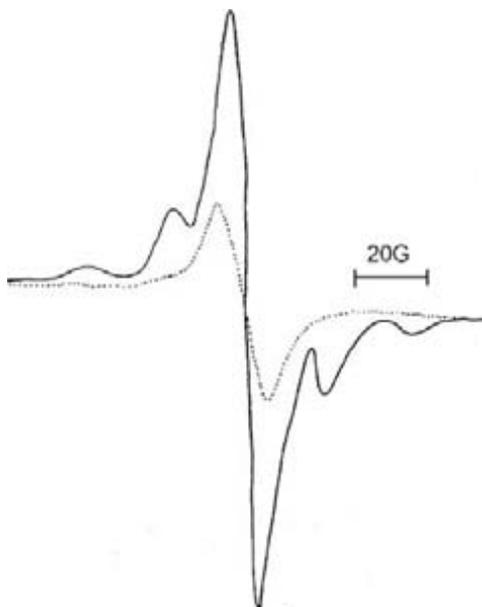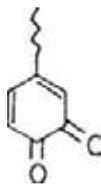compounds were irradiated in a UV-transparent solvent. The UV radiation source had a wavelength of 305–420 nm with peak intensity at 350 nm. They reported that lignin structural units having a saturated propane side chain do not absorb UV radiation; therefore, moieties such as Guaiacylgycerl guaiacyl ether, phenylcoumaran, and pinoresinol probably are not involved in photochemical degradation. The α-carbonyl moiety was the most labile, followed by biphenyl and ring-conjugated double bond structures.

7.2.2 Hydroperoxides

In cooperation with Chang and Feist, Hon showed that the reaction with oxygen to form a hydroperoxide was an integral part of the photo degradation process (Hon et al. 1982). Using singlet oxygen generators and quenchers to investigate the interaction of oxygen under photochemical conditions, they concluded that singlet oxygen was involved in the degradation process and that singlet oxygen quenchers could preclude the formation of hydroperoxides, thereby stabilizing wood against photodegradation. The investigation of the hydroperoxides continued, and in 1992 Hon and Feist reported differences in the hydroperoxide formation at two different UV radiation distributions (>254 nm or >300 nm). Using DRIFT spectroscopy (a combination of diffuse reflectance spectroscopy and Fourier transform infrared spectroscopy), they analyzed the formation and reactions of the hydroperoxides that formed on wood surfaces. The formation of hydroperoxides and carbonyls as well as the destruction of cellulose ether linkages was tracked for up to 180 days of UV radiation exposure. They discussed the energy requirements for bond cleavage in terms of the dissociation energy and proposed mechanisms for the reactions of the hydroperoxides. They also noted that differences in hydroperoxide formation depended on wood species and whether the surface was tangential or radial. These differences were attributed to difference in the wood components and lignin concentration for the various species and grain angles.

   In summary, terrestrial UV radiation (295–400 nm) has sufficient energy to cause bond dissociation of lignin moieties having α-carbonyl, biphenyl, or ring-conjugated double bond structures. A free radical is formed, which then reacts with oxygen to form a hydroperoxide. Additional reactions result in the formation of carbonyls. The degradation process depends on the surface composition of the wood. Lignin absorbs UV radiation throughout the UV radiation spectrum and into the visible light spectrum; however it is only the absorption above 295 nm that is important for weathering of wood (see Figure 7.20). UV radiation at wavelengths shorter than 295 nm are absorbed by the Earth's ozone layer and do not reach its surface.

7.3 REACTION PRODUCTS AND CHEMICAL ANALYSIS

UV radiation at wavelengths below 295 nm can cause degradation not found in normal UV exposure. Barta et al. (1998) used a UV-laser at a wavelength of 248 nm to degrade eight wood species and reported increased carbonyl absorption at 1710–1760 cm^{-1} and decrease aromatic absorptions at 1276 and 1510 cm^{-1}. They also found decreased absorption at 1396, 1465, and 1539 cm^{-1} and
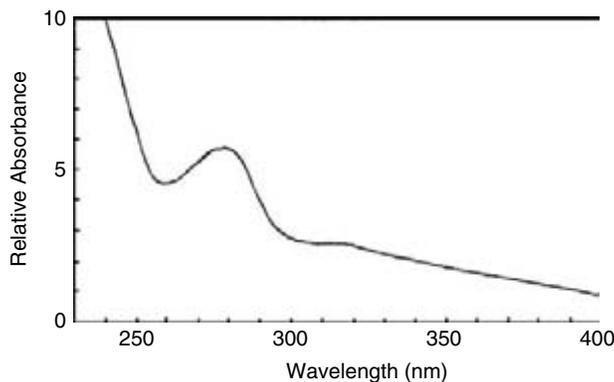
FIGURE 7.20 UV absorption spectra for lignin.

attributed them to changes in lignin, but these changes were not found using conventional xenon arc exposure (UV radiation having filters to approximate the UV radiation at the Earth's surface). Papp (1999) reported that a UV-laser at a wavelength of 248 nm gives completely different results than traditional light sources. Chang (1985) exposed wood to UV radiation and visible light at >220 nm, >254 nm, >300 nm, >350 nm, >400 nm, and >540 nm and reported no lignin degradation at wavelengths above 400 nm.

The infrared spectral analysis of Southern pine (*Pinus sp.*) surfaces at various times as specimens were exposed to UV radiation ($\lambda > 220$ nm) in the laboratory showed a progressive increase in the carbonyl absorption at 1720 and 1735 cm^{-1} and a decrease in absorption at 1265 and 1510 cm^{-1} (see Figure 7.21) (Hon 1983, Hon and Chang 1984). The carbonyl absorption was attributed to the oxidation of cellulose and lignin. The decrease in the absorption at 1265 and 1510 cm^{-1} was attributed to loss of lignin, and this loss was also confirmed by UV absorption spectra of the water-soluble extracts following exposure (see Figure 7.22). Infrared spectra of similar specimens exposed outdoors were distinctly different from the laboratory-exposed specimens (see Figure 7.23) (Hon 1983). The decreased carbonyl absorption and lack of absorption at 1265 and 1510 cm^{-1} was attributed to leaching of the surface by rain as the exposure progressed. No explanation was given for the change at about 1200 cm^{-1}. Gel permeation chromatography of the water soluble extract from the laboratory-exposed specimens showed a molecular weight (M_n) of about 900 Daltons that consisted of carbonyl-conjugated phenolic hydroxyls. They concluded that lignin was the major degradation product. It should be noted that the carbonyl absorptions are rather broad and poorly defined, and one would expect this from the degradation of a complex mixture of polymers. The oxidation undoubtedly occurs at a number of slightly different parts of the lignin.

Periodic FTIR surface analysis of radiata pine during 30 days of outdoor exposure showed perceptible lignin loss in as little as four hours and substantial lignin loss after six days (Evans et al. 1996). Evans (1988) attributed weight loss of specimens during weathering to lignin degradation, not to leaching of water-soluble extractives. Pandey and Pitman (2002) reported degradation in as little as one day of outdoor exposure. Substantial delignification of the surface of radiata pine (*Pinus radiata*) was found after as few as three days of outdoor exposure (Evans et al. 1996).

Hon and Feist (1986) studied the weathering of several hardwood species using UV radiation of ($\lambda > 220$ and > 254 nm) and as with softwoods, there was oxidation of the surface to form carboxyls, carbonyls, quinones, and loss of lignin. The oxidation was confirmed using electron spectroscopy for chemical analysis (ESCA) and showed chemical shifts of C_{1s} from 285.0 eV (carbon-carbon bond) to 287.0 eV and 289.5 eV (carbon-oxygen ether bond and carbon-oxygen carbonyl, respectively).
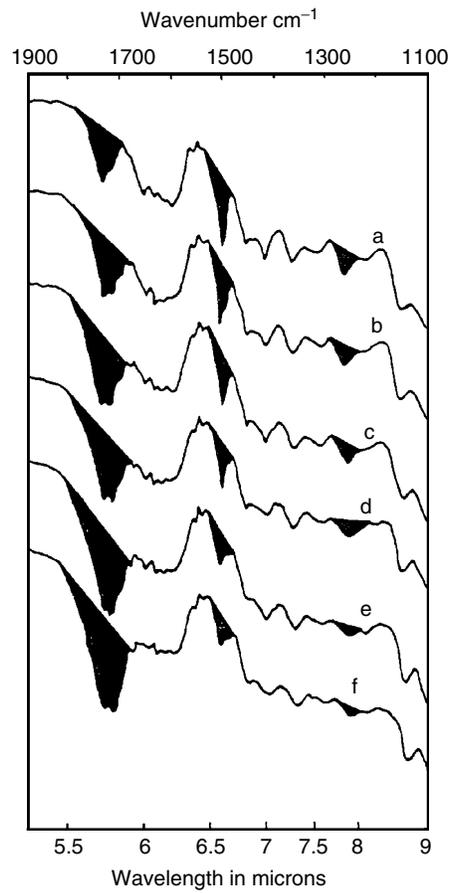
FIGURE 7.21 Infrared (IR) spectra of wood surface following UV irradiation at ≥254 nm; a) control; b) one day; c) four days; d) 10 days; e) 20 days; f) 40 days (Hon 1983).
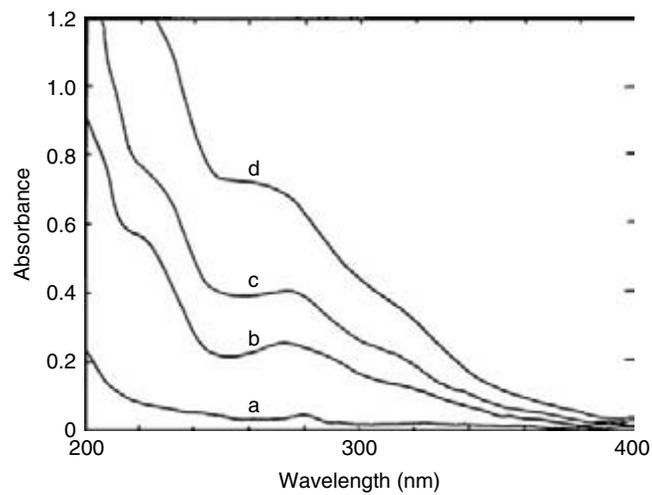

FIGURE 7.22 UV absorption spectra of water extracts of wood following UV irradiation; a) control: b) one day; c) four days; d) 20 days.
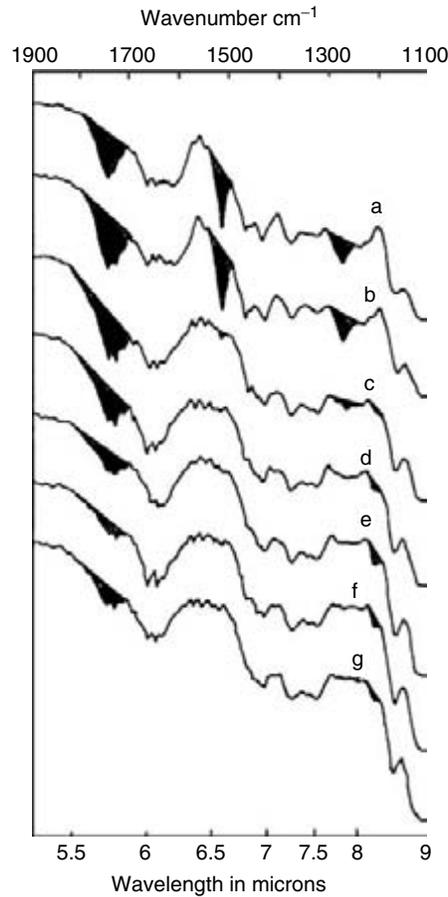
FIGURE 7.23 Infrared (IR) spectra of wood following outdoor exposure: a) control; b) no water leaching; c) 30 days; d) 60 days; e)180 days; f) 300 days; g) 480 days.

Li (1988) evaluated the weathering of basswood (*Tilia amurensis* Rupr.) using ESCA, FTIR, and SEM and found similar results.

Using a xenon light source having borosilicate filters, much sharper carbonyl peaks were observed for the photodegradation of southern pine and western redcedar (*Thuja plicata Donn*) (Horn et al. 1992). The light source used in this work closely matched the natural UV spectra. They also reported the decrease in lignin absorption after exposure and showed that leaching by water was an important component of the weathering. Anderson et al. (1991a, b) also used a xenon light source having borosilicate filters to approximate natural UV radiation. They measured the surface degradation over 2400 hours of UV light exposure with daily water spray of 4 hours, or light without the water spray. Matching specimens were subjected to just water spray for 400 hours. The surface degradation of three softwoods (western redcedar, southern pine, and Douglas-fir) and four hardwoods [yellow poplar, quaking aspen (*Populus tremuloides*), white oak (*Quercus alba*), and hard maple (*Acer saccharum*)] was evaluated using diffuse reflectance FTIR. For the softwoods, the spectra for the three species were quite different before weathering and during weathering with light and water (Anderson et al. 1991a). The absorption at 1730–1740 cm^{-1} increased in intensity during the early exposure then decreased, and the 1514 cm^{-1} decreased. They also reported a rapid
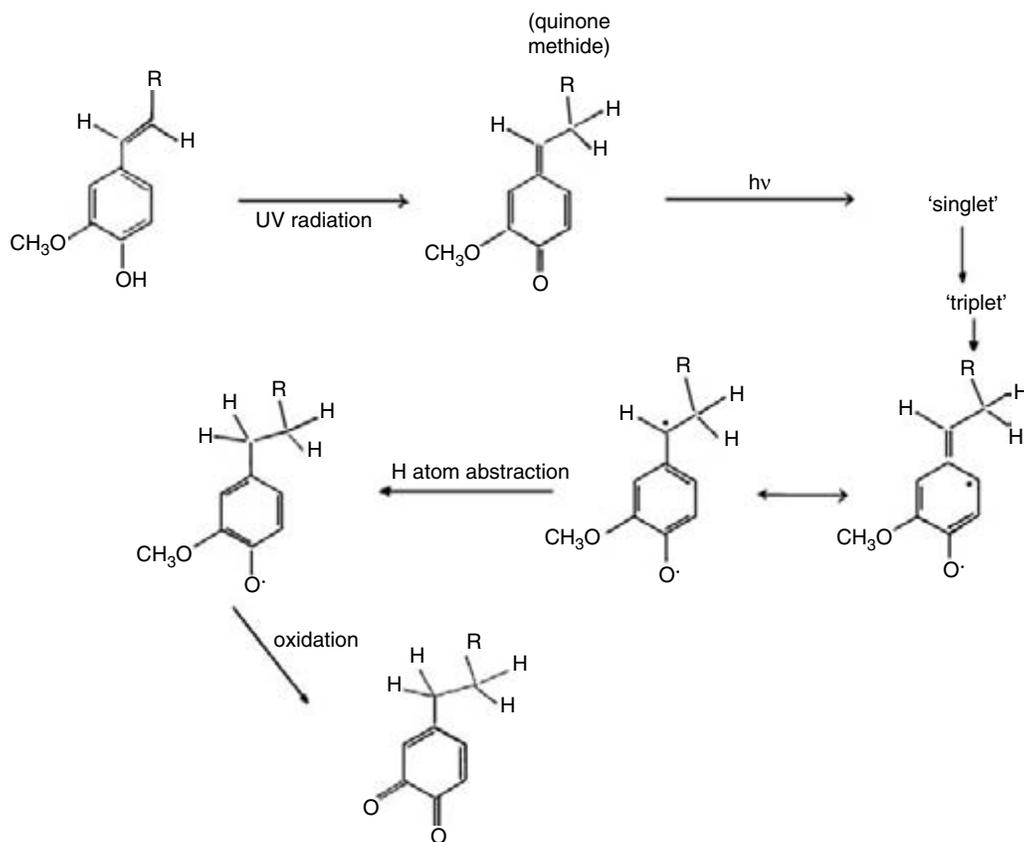
FIGURE 7.24 Lignin photo-oxidation mechanism (Anderson et al. 1991b).

increase in the intensity at 1650 cm^{-1} early in the exposure period, followed by a rapid decrease in intensity; they attributed this to the formation of quinones and quinone methides. All softwood had a distinctly cellulosic spectra following 2400 hours of accelerated weathering (light and water), indicating a loss of lignin. The four hardwoods were slightly different (Anderson et al. 1991b). Yellow poplar and quaking aspen weathered much the same as the softwoods; however, white oak and hard maple weathered slower, probably because of their higher density. As with the softwood, lignin was removed from the surface. A mechanism was proposed (see Figure 7.24). Németh and Faix (1994) used DRIFT FTIR (bands at 1510, 1600, and 1740 cm^{-1}) to quantify the degradation of locust (*Robinia pseudoacacia*) and quaking aspen. In a subsequent study of hardwoods and softwoods, Tolvaj and Faix (1995) reported that the carbonyl absorption was comprised of two sub-bands (1763 and 1710 cm^{-1}) for softwoods, but not for hardwoods. Detailed absorption bands for pine (*Pinus sylvestris*), spruce (*Picea abies*) larch (*Larix decidua*), locust, and poplar (*Populus euramericana*) were reported. Wang and Lin (1991) evaluated the weathered surface of nine Taiwan species following seven years of outdoor weathering in Taiwan using IR spectroscopy. Powders from various depths of the degraded surface were analyzed by transmission (KBr method). IR absorption bands were tabulated.

Košíková and Tolvaj (1998) irradiated *Populus grandis* for 50 hours (UV wavelength was not reported) and isolated the lignin using a series of dioxane, neutral, acid, and base extractions. Difference FTIR spectra (irradiated and unirradiated) of the neutral extracts showed an increase in

OH bands (3500 cm^{-1}), decrease in ring-conjugated carbonyl (1666 cm^{-1}), increase in non-conjugated carbonyl (1747 cm^{-1}), and a decrease in aromatic ring content (1514 and 1593 cm^{-1}). Acid and alkaline extracts showed an increase of carbonyl band (1740 cm^{-1}), and a decrease of aromatic and methoxy groups (1510 and 1270 cm^{-1} respectively).

Mitsui et al. (2001), in studies of color change of spruce and Japanese cypress (*Chamaecyparis obtusa* Sieb. St Zucc), showed that color change of UV irradiated wood was greater when heated than at low temperatures, but at low temperatures the color change was more rapid at high humidity. In a later study, Mitsui (2004) used various filters to study the effect of wavelength on heat-induced color change. He noted differences for color change with and without heat treatment and attributed this to different chemical reactions for UV irradiation at ambient temperature and UV at elevated temperature. The degree of color change increased with decreasing wavelength. Some color change was observed at 400–500 nm and it was attributed to color change of extractives.

It appears that lignin decomposition follows first-order kinetics and is dependent on the wavelength of radiation. High humidity seems to accelerate the degradation.

7.3.1 Depth of Degradation

On the basis of the depth of color change, Browne and Simonson (1957) reported degradation of wood as deep as 2500 μm following exposure to weathering. Later work by Hon and Ifju (1978) and Hon (1981b) showed that this depth was beyond the limit for generation of free radicals. They measured UV radiation and visible light transmission through radial and tangential sections of Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco), redwood (*Sequoia sempervirens* [D. Don] Endl.), Southern pine, and western redcedar sections of various thicknesses in 25-μm steps from 25–300 μm, and the penetration of UV radiation was determined from the presence of free radicals using ESR. They reported that the UV radiation penetrated only 75 μm, whereas visible light penetrated 200 μm. More recent research has shown degradation products beyond the 75 μm limit reported by Hon and Ifju (1978). Horn et al. (1992) studied the penetration of UV radiation and visible light into western redcedar and southern pine. They measured the chemical change using FTIR in 10 μm steps and reported chemical change to about 120 μm. They also noted distinct differences with and without water spray; the water spray removed the degradation products. Kataoka and Kiguchi (2001) examined cross-sections of sugi (*Cryptomeria japonica*) following xenon arc exposure using a micro FTIR technique. Areas as small as 50 μm in cross-section were measured, and the change in the carbonyl (1730 cm^{-1}) and aromatic (1510 cm^{-1}) absorptions were reported at depths of 600–700 μm (see Figure 7.25). Park et al. (1996) reported degradation at depths of 750–850 μm after weathering of hinoki (*Chamecyparis obtusa* Endl.). Wang and Lin (1991) reported the limit to the depth of degradation of 900 μm. Yata and Tamura (1995) found that the depth of wood degradation remained constant after six months of outdoor weathering.

The differences in the reported depth of degradation may be reconciled by considering some of the factors that affect the penetration of UV radiation into wood. The penetration depends on the wood density and the wavelength distribution of the UV radiation and visible light. Denser wood is penetrated less by UV radiation, and shorter wavelengths also penetrate less. The 75 μm limit for UV radiation penetration reported by Hon and Ifju (1978) was determined using a light source having radiation well below 300 nm, whereas the work by Kataoka and Kiguchi (2001) used a UV lamp with radiation above 300 nm. The penetration for these two lights would be quite different, and this might explain the observed differences. The penetration is also dependent on the density, which would be different depending on species and the amount of earlywood and latewood. It was not possible in earlier research to determine UV radiation penetration on a fine enough scale to show the effects of wood anatomy (i.e. earlywood/latewood, radial/tangential gain). It is also possible that the reactions following the generation of the free radical might involve
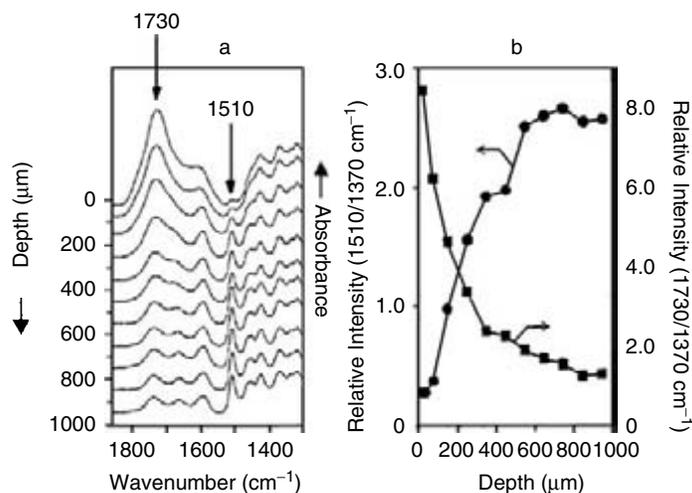
FIGURE 7.25 Fourier transform infrared (FTIR) spectroscopy and selected peak ratios: a) FTIR spectroscopy depth profile of weathered *Cryptomeria japonica*; b) relative peak intensities at 1510 cm^{-1} and 1730 cm^{-1} compared with the intensity at 1370 cm^{-1} (Kataoka and Kiguchi 2001).

chemical moieties deeper into the wood than the depth at which the free radical was generated. The degradation products could also be carried deeper into the wood by the action of water. It was clearly shown that the water-soluble reaction products could be washed from the surface; they might also be washed deeper into the wood. UV radiation sources and filters are now available to do more detailed analysis in future work.

Using FTIR to evaluate grand fir (*Abies grandis*) following exposure to UV radiation, Dirckx et al. (1992) reported different reaction products depending on the wavelength of the UV radiation. They also reported that the hydroxyl absorption decreased as the carbonyl absorption increased, and that the change was dependent on oxygen concentration.

7.3.2 ACID EFFECTS

Williams (1987, 1988) studied the effect of various concentration of sulfuric, sulfurous, and nitric acids on the weathering of western redcedar and found that pH of 2–3 increased the rate of weathering. Park et. al (1996) did a similar study using pH 2 sulfuric acid on hinoki (*Chamaecyparis obtusa* Endl) and evaluated the degradation using SEM. Acid-treated specimens had 1.5 times more degradation of the middle lamella and cell walls than specimens treated with water. Hon (1993) exposed southern pine to UV radiation (≥223 nm) and sulfuric acid spray (pH = 4.4, 3.0, or 2.0) at 65°C and ambient temperatures. He reported increased carbonyl formation and decreased lignin with acid treatment and a slight increase in degradation with increased temperature. His results were similar to previous studies. For most areas of the country, the effect of acid appears to be minor except at pH of 2–3.

In summary, FTIR analysis of degraded wood surfaces show an increase in carbonyl and a decrease in hydroxyl and aromatic content. The oxidation results in cleavage of the lignin at specific locations such as α-carbonyls, and with sufficient degradation, the lignin products are washed from the surface. Oxygen appears to be essential for the reaction, but it was not determined whether it is rate-limiting for the degradation. The increase in the rate of erosion of wood with acid treatment is likely caused by increased hydrolysis of the carbohydrates.
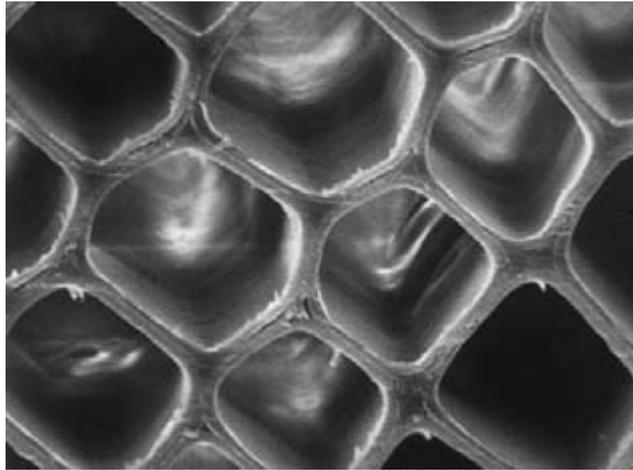
FIGURE 7.26 Southern pine cross-section (1000×).

7.4 PHYSICAL ASPECTS OF DEGRADATION

7.4.1 MICROSCOPIC EFFECTS

7.4.1.1 Destruction of Middle Lamella

As was shown in Chapter 3, Figure 3.8, because the lignin content is higher in the middle lamella than in the cell wall, therefore the photo degradation occurs preferentially in this area of the wood surface. This is particularly noticeable in micrographs of a southern pine cross-section before (Figure 7.26) and after UV exposure (≥220 nm) (Figure 7.27). Hardwood cross-sections (yellow poplar) showed similar degradation (Hon and Feist 1986). Both softwoods and hardwoods degraded at the middle lamella. In addition, the hardwoods degraded at the pores. Yellow poplar was also exposed outdoors and showed similar degradation. The radiant exposure for the laboratory- and outdoor-exposed specimens was not measured; therefore it is difficult to compare the two exposures.
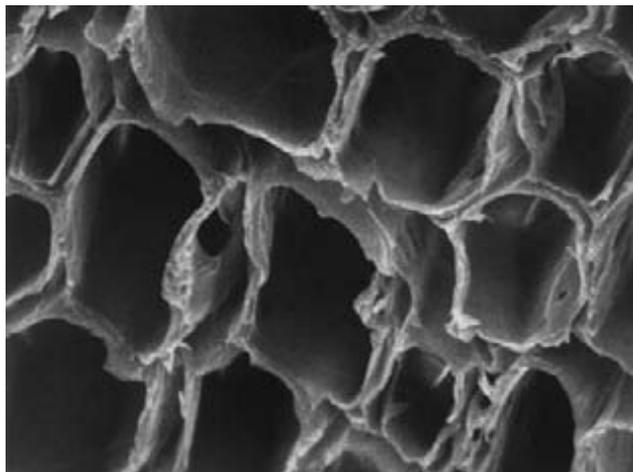
FIGURE 7.27 Southern pine cross-section following 1000 h of UV radiation ($\lambda > 220$ nm, 1000×).
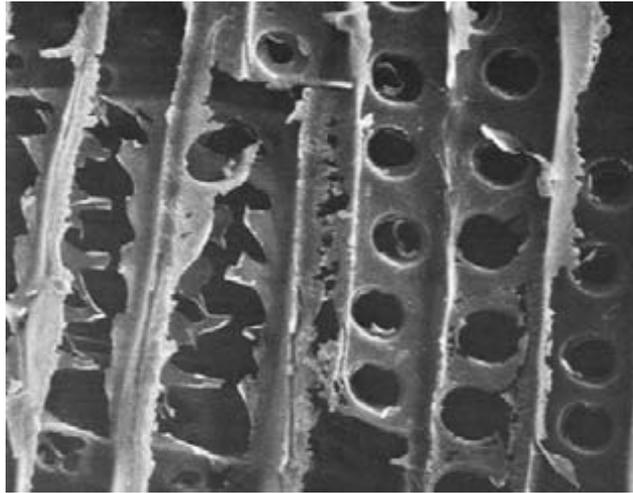
FIGURE 7.28 Deterioration of bordered pits of radial section of southern pine following 1000h of UV radiation (≥220 nm, 1000×).

It should be noted that the wavelength for the laboratory exposure for some of these studies extended well below 295 nm, and the contribution of these high-energy photons can not be determined from these micrographs. Qualitatively, both have degraded in a similar manner. The micrographs from both types of exposure support the premise that the lignin is the photosensitive component in wood.

A number of researchers have shown detailed micrographs of wood at various stages during the weathering of wood. (Leukens and Sell 1972). Kuera and Sell (1987) reported that the degradation around the ray cells in flat-sawn beech was caused by differential dimensional changes between the ray cells and surrounding wood. Kuo and Hu (1991) tracked UV radiation-peak = 254 nm induced degradation of red pine (*Pinus resinosa* Ait.) for 3 to 40 days and showed the progressive degradation from the corners of the middle lamella to the cell wall.

7.4.1.2 Destruction of Bordered Pits and Cell Wall Checking

Micrographs of tangential and radial surface of wood also show lignin degradation (see Figure 7.28). Checks form at the bordered pits and extend aligned with the fibril orientation at a diagonal to the axis of the tracheid. It appears that the lignin binding of the fibrils has been degraded. There is also a separation between the cell walls of two adjacent cells. With extended weathering, cell wall components develop severe checking and the fibrils and tracheids loosen and become detached from the surface. Cross-sectional view of several wood species following more than ten years of outdoor exposure show similar results: There is greater erosion from the earlywood bands and a tendency to check along the earlywood latewood interface for the softwoods (see Figures 7.29a–c). Diffuse porous hardwoods tend to show more even erosion and less checking (see Figure 7.29d).

7.4.2 Macroscopic Effects

7.4.2.1 Loss of Fiber

Much of the information on the rates of wood degradation has been obtained from artificial weathering studies. Futo (1976) exposed wood specimens to UV radiation or thermal treatment and evaluated degradation by weight loss. Using SEM, he noted differences in the microstructure of thermally- and UV-degraded wood (Futo 1976). Williams and Feist (1985) used artificial weathering to evaluate the effects of chromic acid and chromium nitrate treatment of wood surfaces to retard weathering.
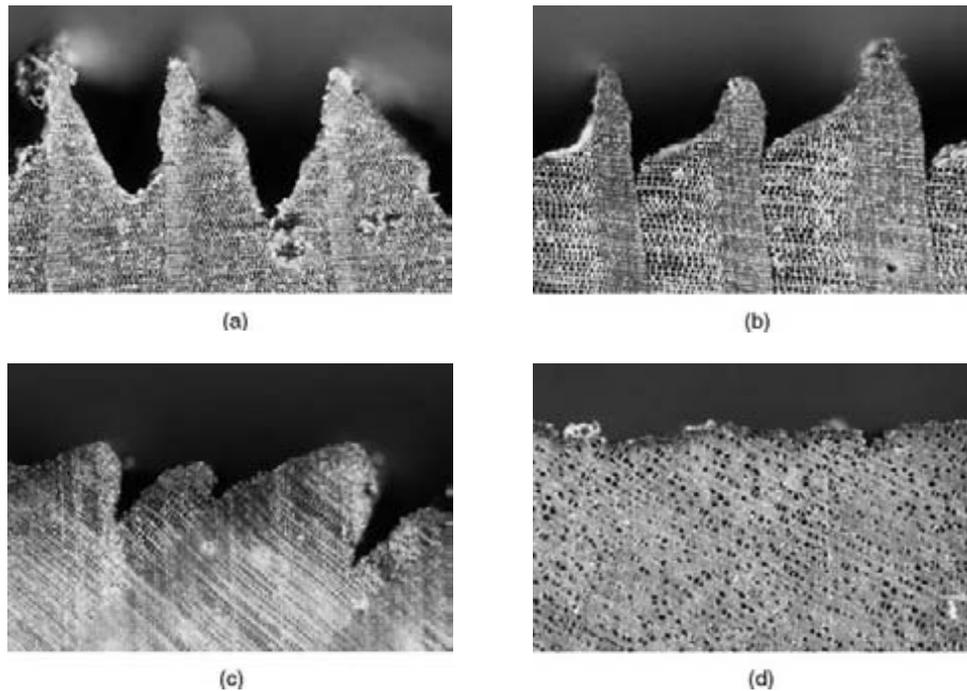
FIGURE 7.29 Micrographs of cross-sections of weathered wood following more than 10 years of outdoor exposure; a) western redcedar; b) Douglas-fir; c) Engelmann spruce; d) red alder.

Williams (1987) used artificial UV radiation to determine the effects of acid on the rate of erosion; degradation was determined by measuring the change in wood mass. Arnold et al. (1991) measured wood erosion of European yew (*Taxus baccata*), Norway spruce (*Picea abies*), southern pine, western redcedar, and white ash (*Fraxinus americana*) during 2400 hours of artificial weathering using xenon arc with borosilicate filters and fluorescent UV chambers. Both were equipped with water spray. They obtained similar results with both chambers and noted that water spray was essential for simulating natural weathering. Derbyshire et al. (1997) used artificial weathering to determine the activation energies for several wood species; wood degradation was determined by loss of tensile strength.

Derbyshire and Miller (1981) exposed thin strips of Scots pine and lime (*Tilia vulgaris*) for up to 24 weeks outdoors under various filters to give wavelengths >300 nm, >350 nm, >375 nm, and >400 nm and measured the tensile strength. They reported that visible light (≥400 nm) contributed to the degradation. From measurement of the cellulose disperse viscosity of weathered and unweathered specimens, they concluded that there was cellulose degradation on specimens exposed to the total solar spectrum. Scanning electron micrographs of the failed specimens clearly show the degraded wood components. Derbyshire et al. (1995a) also used accelerated weathering to degrade specimens and used short-span tensile tests to evaluate degradation. In a second study by Derbyshire et al. (1996), 0-span and 10mm-span tensile tests were conducted on six softwood species. The drop in the strength was plotted against UV radiation dose and the difference in strength between the 0-span and 10mm-span was attributed to degradation of different components of wood. The 0-span test measured the cellulose strength, whereas the 10-mm span measured the wood strength. An exponential expression for the degradation was proposed and compared with the experimental data. In a third study (Derbyshire et al. 1997), they showed that the degradation of ten wood species was temperature dependent; linear Arrhenius plots had activation energies of 5.9–24.8 kJ/mol. On the basis of 0-span and 10mm-span tensile tests and SEM data, Derbyshire et al. (1995b, 1996) attributed

the degradation to three phases in which the first phase was a slow surface structural change and the other two phases were rapid degradation of lignin and cellulose. They also compared the degradation of six softwood species and developed a mathematical expression that fit strength loss of thin sections of wood following short period of natural weathering. (Derbyshire et al. 1996)

Researchers have compared the results of natural and accelerated weathering. Feist and Mraz (1978) found good correlation between erosion rates from natural and accelerated weathering. These researchers also found good correlation between erosion rate and wood density. They reported similar erosion rates for earlywood and latewood for some species after an initial two-year period. Deppe (1981) compared 12- to 60-week accelerated weathering with 3- to 8-year natural weathering of wood-based composites, but he was primarily interested in water absorption, thickness swelling, and strength properties. Derbyshire et al. (1995a, b) compared natural and artificial weathering by assessing the degradation of small strips of wood. Evans (1988) also evaluated the degradation of thin wood veneers exposed outdoors for up to 100 days, using "weight loss" as the unit of measurement. Sell and Leukins (1971) weathered 20 wood species outdoors for one year at 45° south, but their main interest was in the discoloration of wood. Evans (1989) used SEM to show the loss of wood, primarily degradation of the middle lamella, following two years of natural weathering. Yoshida and Taguchi (1977) noted loss of strength in plywood exposed to natural weathering for seven years, and Ostman (1983) measured the surface roughness of several wood and wood-based products after four years of natural weathering. Bentum and Addo-Ashong (1977) evaluated cracking and surface erosion of 48 timber species, primarily tropical hardwoods, after five years of outdoor exposure in Ghana. Weathering characteristics of tropical hardwoods from Taiwan during both natural and accelerated weathering have also been reported (Wang 1981, 1990; Wang et al. 1980). Williams et al. (2001d) used accelerated weathering to evaluate the erosion rates of several tropical hardwoods from Bolivia.

In a series of outdoor studies spanning 16 years, Williams and coauthors reported on the effects of surface roughness, grain angle, exposure angle, and earlywood/latewood on weathering rates of several softwood and hardwood species (Williams et al. 2001a, b, and c). Erosion rates for earlywood and latewood were reported for several plywood and lumber species (see Table 7.5). For all wood species, erosion rates for earlywood and latewood differed greatly during the first seven years of weathering. For Douglas-fir and southern pine, significant differences continued after seven years. However, for western redcedar and redwood, erosion rates were generally the same after seven years. Because of this change in the erosion rate at seven years, the rates from 8–16 years may be more representative of long-term erosion rates (see Table 7.6). The erosion rate of vertical-grained lumber was considerably higher than that of flat-grained plywood. Only slight differences were observed for saw-textured as opposed to smooth plywood. The erosion rates confirmed the effect of wood-specific gravity, showing that more dense species weather more slowly. The density difference also affects the erosion rates of earlywood and latewood (see Figures 7.29a–c). The figure clearly shows more earlywood erosion for western redcedar than for Douglas-fir and Engelmann spruce. The erosion rate for vertical-grained wood varied from 4.5 μm/yr for southern pine to 9.5 μm/yr for western redcedar and plywood was slightly less.

In the second study in the series by Williams et al. (2001b), the erosion rates for ponderosa pine (*Pinus ponderosa*, Dougl. ex Laws), lodgepole pine (*Pinus contorta*, Dougl. ex Loud.), Engelmann spruce (*Picea engelmannii*, Parry ex Engelm.), western hemlock (*Tsuga heterophylla*, (Raf.) Sarg.), and red alder (*Alnus rubra*, Bong.) measured over ten years are shown in Table 7.7. The average erosion rates for earlywood and latewood for ponderosa pine, lodgepole pine, Engelmann spruce, and western hemlock varied from 40 to 50 μm/yr. This is slightly less than the erosion rate usually given for softwoods. The erosion rate for earlywood alone was less than 60 μm/yr. The erosion rate for red alder earlywood, 58 μm/year, was the same as that for western hemlock earlywood, which is not surprising given the similar specific gravity of these species. The thin latewood bands of red alder broke off as the earlywood eroded and had little effect on the rate of

TABLE 7.5
Erosion of Earlywood and Latewood on Smooth-Planed Surfaces of Various Wood Species after Outdoor Exposure near Madison, Wisconsin[a]

Wood Species	Avg SG[b]	Erosion (μm) after Various Exposure Times[c]											
		4 years		8 years		10 years		12 years		14 years		16 years	
		LW[d]	EW[d]	LW	EW	LW	EW	LW	EW	LW	EW	LW	EW
Western redcedar plywood	—	170	580	290	920	455	1,09	615	1,16	805	1,355	910	1,475
Redwood plywood	—	125	440	295	670	475	800	575	965	695	1,070	845	1,250
Douglas-fir plywood	—	110	270	190	390	255	500	345	555	425	770	515	905
Douglas-fir	0.46	105	270	210	720	285	905	380	980	520	1,300	500	1,405
Southern pine	0.45	135	320	275	605	315	710	335	710	445	1,180	525	1,355
Western redcedar	0.31	200	500	595	1,09	765	1,32	970	1,56	1,16	1,801	1,380	1,945
Redwood	0.36	165	405	315	650	440	835	555	965	670	1,180	835	1,385

[a] Specimens were exposed vertically facing south. Radial surfaces were exposed with the grain vertical.
[b] SG is specific gravity.
[c] All erosion values are averages of nine observations (three measurements of three specimens).
[d] EW denotes earlywood; LW, latewood.

TABLE 7.6
Typical Erosion Rates for Various Species and Grain Angles for 8–16-Year Outdoor Exposure near Madison, Wisconsin[a]

Species, Wood, and Orientation	Earlywood Erosion[b] (μm/year)	Latewood Erosion[b] (μm/year)	Avg Erosion (μm) per Year[c]	Erosion (mm) per 100 Years
Western redcedar				
Lumber, vertical	101.5	91.5	95	9.5
Plywood, flat	66.5	75.5	70	7.0[d]
Redwood				
Lumber, vertical	84.5	67.5	75	7.5
Plywood, flat	65.0	56.0	60	6.5[d]
Douglas-fir				
Lumber, vertical	77.0	44.0	60	6.0
Plywood, flat	60.0	43.0	50	5.0[d]
Southern pine				
Lumber, vertical	59.5	34.0	45	4.5[e]

[a] For Southern Pine, erosion rates were determined from slope of regression line from 0- to12-year data.
[b] Average of erosion rates for vertical and horizontal (flat) grain exposures.
[c] Average of earlywood and latewood erosion rates rounded off to nearest 5 units.
[d] The face veneer would be gone long before 100 years had passed.
[e] Specimens were decayed after 12 years of exposure.

TABLE 7.7

Typical Erosion Rates for Earlywood and Latewood for Various Species Measured during 10 Years of Outdoor Exposure near Madison, Wisconsin[a]

Species	Earlywood (μm/yr)	Latewood (μm/yr)	Average Erosion (μm) per Year[b]	Erosion (μm) per 100 Years[c] (mm)
Ponderosa pine	42	35	40	4.0
Lodgepole pine	49	33	40	4.0
Engelmann spruce	54	38	45	4.5
Western hemlock	58	39	50	5.0
Red alder	58	—	60	6.0

[a] Data from vertical and horizontal grain exposures were combined to compute earlywood and latewood erosion rates.

[b] Average erosion of earlywood and latewood rounded to nearest 5 units.

[c] Extrapolated from average earlywood and latewood erosion rates rounded to nearest 0.5 mm.

erosion (see Figure 7.29d). Differences in surface morphology were shown to affect weathering of the surface. Wood species with wide latewood bands weathered differently than did species with thin latewood bands (see Figure 7.29a–d).

Erosion rates were also determined for Douglas-fir, loblolly pine (*Pinus taeda* L.), southern pine, western redcedar, northern red oak (*Quercus rubra* L.), and yellow-poplar for different angles of exposure (see Table 7.8) (Williams et al. 2001c). The erosion rates of all species were considerably higher at the 45° angle of exposure than at 90°. For many species, erosion was about twice as fast for the 45° exposure. Most species showed little difference in erosion between the 0° and 45° exposures. Although UV radiation is higher for horizontal specimens (0° exposure), the authors hypothesize that the decrease in the washing action of water and the build-up of degradation

TABLE 7.8

Typical Erosion Rates for Earlywood and Latewood of Various Species during 6 Years of Outdoor Exposure near Madison, Wisconsin, at Different Exposure Angles[a]

Species	Earlywood (μm/year)			Latewood (μm/year)			Average Erosion[b] per 100 Years (mm)		
	90°	45°	0°	90°	45°	0°	90°	45°	0°
Douglas-fir	42	97	81	20	42	48	3	—	—
Loblolly pine	34	78	89	20	44	39	2.5	—	—
Southern pine	62	123	102	20	48	44	—	—	—
Western redcedar	131	177	135	26	96	77	—	—	—
Northern red oak	35	67	114	30	80	105	3	7.5	11
Yellow-poplar	48	117	209	—	—	—	—	—	—

[a] Data from vertical grain (radial surface) exposure of earlywood and latewood.

[b] Extrapolation of average of earlywood and latewood erosion rounded to nearest 5 units. Where the difference in erosion rate between earlywood and latewood was large, average erosion is not given.

products and dirt on the surface probably protected these specimens to some extent. More rapid degradation at 0–45° would be expected to have a great effect on the service life of wood products used for roofing and decks. The average erosion rate for Douglas-fir and loblolly pine (earlywood and latewood) exposed at 90° was about 30 and 25 μm/year respectively, considerably less than that for softwoods such as ponderosa pine, lodgepole pine, Englemann spruce, and western hemlock.

Evans measured weight loss of thin veneers of radiata pine following 50 days of outdoor exposure at various exposure angles and reported the following: 90° (vertical), 17.0%; 70°, 26.5%; 60°, 29.4%; 45°, 31.8%; and 0°, 34.1% weight loss. Seasonal effects cause slower erosion in the winter. (Raczkowski 1980; Evans 1996). Groves and Banana (1986) used SEM studies to determine the degradation of radiata pine exposed up to six months in Australia.

7.4.2.2 Grain Orientation

In a detailed study of the effects of grain angle on weathering of Scots pine and Norway spruce (*Picea abies* Karst.) following 33 months outdoors, Sandberg (1999) reported the following: Pine had 13 and spruce 6 times more total checking per unit area on the tangential versus radial surface; tangential surfaces had deeper checks; CCA and linseed oil treatment had only minimal effect to decrease checking; on radial surfaces, checking occurred primarily at the latewood/earlywood border; degradation of bordered pits was a distinct difference between radial and tangential surfaces; and the microfibrils in the S_2 layer are the most weather resistant component.

7.4.2.3 Water Repellency

As wood weathers, the extractives are leached from the surface and it becomes less water-repellent. The loss of lignin also makes the surface more hydrophilic. Contact angle measurements on weathered western redcedar dropped from 77° to 55° after four weeks of outdoor weathering (Kalnins and Feist 1993). Kang et al. (2002) also reported increased wettability for Sitka spruce exposed to xenon arc radiation and water spray.

7.4.2.4 Checks and Raised Grain

In addition to the slow erosion of the wood surface as wood weathers, the surface also developed checks and raised grain. This type of degradation is often more severe than erosion. For example, wood decks are often replaced long before their expected service life because of raised grain and splitting. This degradation is caused primarily by moisture. A cross-section view of weathered wood surfaces for several wood species after ten years of outdoor weathering clearly shows the formation of checks (Figures 7.29b and c). The check often forms at the earlywood/latewood interface as shown for southern pine and Douglas-fir. On flat-grained surfaces, checking occurs predominately on the bark side; however, the raised grain on the pith side can be a more severe problem. Both checking and raised grain result from the wetting and drying of wood that occurs from precipitation and daily and seasonal changes in RH. As was found from the study of Bolivian hardwoods, the erosion rate for many of the species was extremely slow, but after 20–30 wet/dry cycles, they developed severe checking (Williams et al. 2001d).

Water in the absence of UV radiation or light can cause strength loss of wood veneers (Banks and Evans 1984; Evans and Banks 1988; Voulgardis and Banks 1981). Scots pine (*Pinus sylvestris*) and lime (*Tilia vulgaris*) veneers were soaked in deionized water at 50°C and 65°C; SEM of specimens following tension tests showed different failure modes for the soaked specimens compared with controls that had not been soaked. Controls failed by fracture across the cell wall, whereas the veneers that had been soaked failed by inter-fibril sheer. Chemical analysis of wood flour that had been placed in 65°C water for 50 days showed a loss of hemicellulose and lignin, but not cellulose (Evans and Banks 1990). It seemed likely that hydrolysis of the hemicelluloses

had occurred. In subsequent studies using radiata pine (Evans et al. 1992), mannose and xylose were isolated from water extracts from weathered wood. Analysis of the holocellulose following weathering showed depletion of mannose, xylose, arabinose, and galactose. Following outdoor exposure, methanol and hot water extracts of weathered wood yielded 6.4% and 18.0% soluble components respectively, whereas unweathered wood had only 1.6% and 2.2%. They attributed the increased solubility to degradation of the lignocellulose matrix.

During outdoor weathering, water mechanically abrades the surface and washes away degradation products. In addition, water probably hydrolyzes hemicelluloses, particularly at the surface. As the lignin degrades, the hemicelluloses become more vulnerable to hydrolysis. Sudiyani et al. (1999b) reported that water was instrumental in the decomposition of the lignin in addition to washing away the reaction products.

The effects of iron in contact with wood during laboratory weathering that included moisture, freezing, heat, UV radiation, and fatigue cycling caused 25% more creep in specimens exposed to iron than those without iron contact. (Helinska-Raczkowska and Raczkowski 1978). It seems the iron compounds can catalyze moisture-induced degradation. Raczkkowski (1982) reported that iron in contact with beech (*Fagus sylvatica*) increased the degradation during laboratory exposure to cyclic moisture, temperature, and UV radiation, but that beech modified by *in situ* polymerization of styrene retarded degradation. Hussey and Nicholas (1985) reported that hindered amine light stabilizers inhibited the iron/water degradation of wood. In tensile tests of specimens exposed to water, water/iron, water/iron/stabilizer and controls, the stabilized specimens had greater tensile strength than both the water- and water/iron-exposed specimens.

In summary, the erosion rate depends on the anatomy of the wood, grain angle, density, and angle of exposure. In general, most softwoods erode at a rate of 6 mm/century and hardwoods at 3 mm/century. In addition to UV radiation, water causes degradation. Water abrades the surface, washes away reaction products, hydrolyzes carbohydrates, and causes checking and raised grain.

7.4.3 Weathering of Wood/Wood Composites

Wood composites, such as plywood, fiberboard, flake-board, and particleboard, are vulnerable to degradation. As with solid wood, the surface of these products undergoes photochemical degradation. Composites comprised of wood bonded to wood, whether made with veneers, flakes, or particles, are much more vulnerable to moisture cycles than is solid wood.

Exterior grades of plywood are manufactured from veneers that are rotary-peeled from logs. This process yields a veneer that is flat-grained, and the peeling process forms lathe checks in the veneer. When the surface veneers are put in place to from the plywood, the surface having lathe checks is placed facing the inner veneer. The lathe checks are not visible on the surface, but the veneer has internal flaws. As plywood weathers, these lathe checks grow to the surface to form parallel-to-grain cracks in the surface veneer. As shown in Tables 7.5 and 7.6, plywood surfaces erode slightly slower than solid wood of the same spe cies, but it is the development of surface cracks that limit the service life of unprotected plywood. It is the moisture cycles that cause these cracks to form. If plywood is not protected with a finish, it can fail within ten years (see Figure 7.30). The figure shows a western redcedar plywood panel after eight years. The left part of the panel was protected by a batten and is not weathered. About half the thickness of the surface veneer has eroded and there are numerous cracks in the face veneer. Plywood must be protected with a finish. Surface checking and cracking of surface veneers also occurs on laminated veneer lumber (Hayashi et al. 2002). Yoshida and Taguchi (1977a, b) determined the decrease in thickness and mechanical properties of three- and five-ply red luan (*Shorea sp.*) and three-ply kapur (*Dryobalanops* sp.), Shina (basswood: *Tilia sp.*), and kaba (birch: *Betula sp.*) following seven years of outdoor exposure. Surface checks primarily affected shear strength of the panels. The erosion of the surface decreased static and impact bending strength. Five-ply panels had slightly higher erosion rates, compared with three-ply panels of the same species.
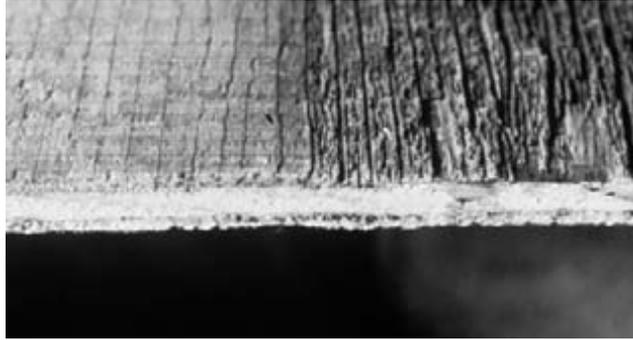
FIGURE 7.30 Western redcedar plywood following 8 years of outdoor exposure (left-half was protected by a batten).

As with plywood, flake-board, fiberboard, and other types of particle boards are extremely vulnerable to moisture cycles. As they weather, the surface flakes or particles debond and fall off. They must be finished with a multi-coat paint system if they are to be used outdoors.

7.4.4 WEATHERING OF WOOD/PLASTIC COMPOSITES

Wood/plastic composites are less susceptible to moisture cycles than wood composites, but are degraded by UV radiation and are more sensitive to heat (see Chapter 13). During weathering of wood/high density polyethylene (wood/HDPE) composites, such as decking, thermal degradation of the polyethylene component is an important factor and can be described by first-order kinetics with an activation energy of 23.2 kJ/mol (Li 2000). In addition to the thermal effects on the HDPE component, wetting and drying of the wood component causes the HDPE to crack. Li reported that these effects cause more damage than photo-oxidation. Bending tests of kanaf-filled HDPE following 2000 hours of xenon arc weathering showed significant decreases in bending strength and stiffness (24% and 42%, respectively) (Lundin et al. 2002). Wood flour-filled HDPE showed similar results; strength and stiffness decreased 20% and 33% respectively.

Stark and Matuana (2002) exposed various formulations of wood-flour/HDPE composites and HDPE to 2000 hours of xenon arc weathering. They reported that hindered amine light stabilizers (HALS) did improve color stability and mechanical properties. The wood/HDPE composites maintained flexural modulus of elasticity (MOE) until about 2000 hours of weathering, whereas the HDPE showed decreased MOE after 1000 hours. Matuana et al. (2001) reported that rutile titanium dioxide was an effective UV stabilizer for wood/PVC composites.

Matuana and Kamdem (2002) reported that the wood in wood/polyvinyl chloride (wood/PVC) composites was an effective chromosphore; wood/PVC degraded faster than PVC (QUV weathering with water spray). Degradation was evaluated using DRIFT-FTIR and ESCA. In contrast, Lundin et al. (2002) reported that weathered wood/PVC specimens showed no loss in strength or stiffness (tension tests), but the unfilled PVC lost almost 50% of its strength after only 400 hours of weathering. They attributed the improved mechanical properties to load-bearing properties and stress transfer of the wood flour. Stark et al. (2004) compared the weathering of injection-molded, extruded, and extruded then planed 50% wood/HDPE specimens. They showed that the manufacturing method affected the surface composition. Planed specimens had a higher wood component at the surface than the injection-molded or extruded specimens and had higher degradation during the first 1000 hours of xenon arc weathering with water spray.

Rowell et al. (2000) used xenon-arc/water-spray weathering cycle (2000 hours) to evaluate the effect of fiber content in an aspen/polyethylene composites (fiber loading of 0, 30–60%, by weight). As the fiber content increased, the weight loss increased, but at the conclusion of the 2000 hours, after the degraded surface was scraped from the surface, the weight loss was greater for the polyethylene with no wood fiber. It seems that the polyethylene degradation products are not washed from the surface during weathering as are the wood degradation products.

These studies exemplify the importance of the surface composition on weathering and the importance of water in the process. Composites having a high concentration of wood fibers at the surface can absorb water, whereas surfaces having fibers encapsulated by HDPE cannot absorb water until the HDPE has degraded.

7.4.5 Effects of Biological Agents

It is generally accepted that mold (mildew) such as *Aureobasidium pullulans*, the most common microorganism found on weathered wood, does not have the enzymes to degrade lignin or polysaccharides. However, the blue stain fungus (*Diplodia natalensis*) caused more strength loss to Lime (*Tilia vulgaris* Hayne) specimens weathered for 30 days compared with specimens that had not been inoculated with the fungi. (Evans and Banks 1986) In general, molds cause more appearance problems than actual degradation of wood; however, aggressive cleaning methods to remove them using strong chemicals and/or power-washing can greatly accelerate the loss of wood fiber from wood surfaces.

7.4.6 UV Degradation of Tropical Woods

Researchers have reported the degradation of several tropical wood species. Fuwape and Adeduntan (1999) reported the weight loss of Gmelina (*Gmelina arborea* Roxb.) weathered outdoors. Nakamura and Sato (1978) evaluated the degradation of red-lauan, kapur, shinanoki, and kaba (botanical names not given in paper) plywood after seven years of outdoor exposure. Onishi et al. (2000) reported on the degradation of 12 species following 2 years of outdoor exposure. Wang (1981) and Wang et al. (1980) reported strength loss of 18 Taiwan wood species exposed to four years outdoor exposure and accelerated weathering. The degradation was measured by static and impact bending tests. The strength decreased linearly with time of exposure.

7.4.7 Paint Adhesion

Williams et al. (1987) preweathered western redcedar for 0, 1, 2, 4, 8, and 16 weeks prior to painting. They reported that two to four weeks of weathering of western redcedar prior to painting caused up to 50% loss in paint adhesion. Matched specimens were placed outdoors. After 17 years exposure, the paint on the controls (0 weeks preweathering) was in almost perfect condition, whereas the paint on all preweathered panels was degraded. The longer the wood was preweathered, the poorer the paint (Williams and Feist 2001). Underhaug et al. (1983) reported that one month of wood weathering prior to painting lead to paint failure within 6 to 10 months. Kleive (1986) reported poor performance of paint when refinished after up to 4 years weathering. Williams and Feist (1993) reported premature failure of paints and solid-color stains that were weathered prior to finishing. Williams and Feist (1994) reported on the service life of semitransparent stains, acrylic latex paints, alkyd paints, and solid-color stains applied to Engelmann spruce (*Picea engelmannii*), yellow poplar (*Liriodendron tulipifera*), southern pine (*Pinus* sp.), and sweetgum (*Liquidambar styraciflua*). Wood substrates were weathered for 4, 8, and 12 weeks prior to applying the finishes. The type of finish had the greatest effect on service life, followed by surface roughness, type of substrate, and finally the amount of preweathering.

7.5 CHEMICAL TREATMENTS TO RETARD WEATHERING

7.5.1 Chromic Acid

Chromic acid is an aqueous solution of chromium trioxide (CrO_3); the chromium is in its +6 oxidation state. Treatment of wood with 5–10% chromic acid gives a surface that is highly resistant to photochemical degradation. The chromic acid treatment also gives a surface that is water repellent. Aqueous solutions of other chromium VI compounds such as sodium dichromate also retarded the weathering of wood. The benefits of the treatment were investigated in detail by Black and Mraz (1974) and later by Feist (1979) and the mechanism was studied by Pizzi (1981a,b) and Williams and Feist (1984). Numerous references to other work are contained in these publications. More recent work has shown similar effects (Li et al. 1989, Pandey and Khali 1998; Pandey and Pitman 2002). Chromium oxidizes wood components and in the process is reduced to chromium III (+3 oxidation state). Cr (VI) forms tetrahedral coordination compounds and when it is reduced to Cr (III), it becomes octahedral. With ample sites for coordination with either lignin or carbohydrates, chromium forms a highly insoluble complex with wood, cellulose, or lignin model compounds. In essence, it becomes a integral part of the wood surface. This complex greatly retards photochemical degradation. Chang et al. (1982) compared chromic acid treated and untreated southern pine following exposure to artificial UV radiation (see Figures 7.26 and 7.27). The untreated specimens clearly show degradation of the middle lamella and cell wall. Chromic acid-treated specimens show almost no degradation (see Figure 7.31). The mechanism by which chromic acid treatment protects wood has not been determined; however, the important characteristics are that a chromium complex is formed at the surface, the complex is insoluble, and the complex interferes with the photochemical pathway. Williams and Feist (1984) used ESCA to evaluate the oxidation of the surface of wood and cellulose and showed that cellulose was slightly degraded by the chromic acid treatment and gave off CO_2 following chromic acid treatment. ESCA evaluations of wood treated with chromic acid were also reported by de Lange et al. (1992). They also reported decarboxylation of cellulose and confirmed the stabilization of lignin by chromium complexes.

Guajacol was used as a lignin model compound to study the reactions of chromic acid with wood. It forms an insoluble polymeric complex and Pizzi and Mostert (1980) attributed the waterproofing of wood by chromic acid to the formation of chromium complexes with lignin. Kubel and Pizzi (1981) reported similar waterproofing with other metal oxides that form water-insoluble complexes with
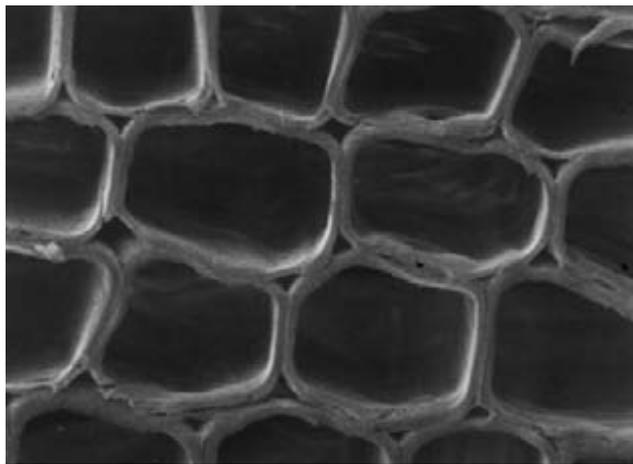

FIGURE 7.31 Southern pine cross-section treated with 5% chromic acid following 1000 hours UV radiation (≥220 nm, 1000×).

guajacol. The reaction kinetics have been determined and the rate constant and activation energies agree well with the rates of chromic acid reactions with wood. Pizzi and Mostert (1980) and Schmalzl et al. (1995) characterized the reaction products of guaiacol with aqueous solutions of ferric chloride and chromic trioxide. Both compounds gave complex mixtures of guaiacol oligomers, however chromium complexes were highly insoluble, thermally stable, and acted as a screen against UV radiation (Schmalzl et al. 2003).

Chromic acid also reacts with pure cellulose to form a waterproof complex. (Williams and Feist 1984) It seems that chromic acid can react with both lignin and polysaccharides to waterproof wood.

Evans and Schmalzl (1989) and Derbyshire et al. (1996) used 0-span tensile tests of thin veneers to determine strength loss. The strength loss following outdoor weathering was attributed to degradation of the cellulose components in wood. Evans and Schmalzl (1989) compared the strength loss with weight loss following weathering and found that chromic acid-treated wood had about the same 0-span strength loss as untreated controls, but the weight loss was significantly less. Image analysis scanning election micrographs of checking at bordered and half-bordered pits following weathering was used as a means to quantify the effect of chromic acid and aqueous solutions of ferric chloride and ferric nitrate treatment of wood. (Evans et al. 1994) It is known that chromic acid causes degradation of cellulose (Williams and Feist 1984) and the 0-span tensile test confirms this. The chromic acid protects the lignin; therefore, the weight loss is less for the chromic acid-treated specimens.

7.5.2 Chromated Copper Arsenate Preservatives

Southern pine pressure treated with chromated copper arsenate (CCA) eroded slower than similar wood treated with brush-applied chromic acid. (Feist and Williams 1991) The higher penetration and retention of chromium in the pressure-treated wood gave better protection. Others showed similar effects (Chang et al. 1982, Williams and Feist 1984, Hon and Chang 1984, Evans 1992).

7.5.3 Copper-Based Preservatives

Using FTIR to monitor the lignin degrade (1510 cm^{-1}) and formation of carbonyls (1720–1740 cm^{-1}), Liu et al. (1994) reported that 2% ammoniacal copper quat (ACQ) preservative treatment of southern pine sapwood retarded wood degradation more than 2% CCA treatment. The specimens were exposed for 35 days outdoors and evaluated weekly. In a similar study, treatment with didecyldimethyl ammonium chloride (DDAC) performed worse than the controls, while the ACQ retarded degradation (Jin et al.1991).

7.5.4 Chemically Bonded Stabilizers

On the basis of the studies using chromic acid, Williams (1983) investigated organic stabilizers that bonded to wood. Chemically reacting a UV absorber having an epoxy moiety [2-hydroxy-4-(2,3 epoxypropoxy)benzophenone] to the wood surface retarded the erosion rate and gave improved performance to clear coating applied over the modified surface. Kiguchi (1992) did additional work using the same treatment on several Japanese wood species and reported similar results.

7.5.5 Commercial Stabilizers

Hon et al. (1985) prepared benzophenone-containing monomers using glycidyl methacrylate to form 2-hydroxy-4 (3-methacryloxy-2-hydroxy propoxy) benzophenone. Polymeric coatings using this monomer improved color stability of southern pine. The UV stabilizer was not bound directly to the wood. They also prepared mixtures of several commercial stabilizers in the coatings. Treatments also included several penetrating mixtures of PEG-400 with 1-octadecanol, which improved color retention. It should be noted that the UV exposure included wavelengths below 295 nm and

did not have water spray. Additional work was done using these chemicals and exposing the specimens at the same wavelengths by Panda and Panda (1996). They reached the same conclusions.

7.5.6 CHEMICAL MODIFICATION

Rowell et al. (1981) and Feist and Rowell (1982) reacted southern pine sapwood with either butylene oxide or butyl isocyanate as a cell wall modification (see Chapter 14) or with *in situ* polymerized methyl methacrylate as a lumen filler (see Chapter 15). Specimens that had only butylene oxide or butyl isocyanate cell wall modification degraded at the same rate as the unmodified specimens under xenon arc accelerated weathering, but the methyl methacrylate lumen fill decreased the rate. The best results were obtained using both lumen fill and cell wall modification—these specimens degraded at half the rate of the controls. The cell wall modification made the wood dimensionally stable, and the lumen fill helped hold degradation products in place, thus improving UV resistance. Similar results were obtained using acetic anhydride to modify the cell wall and methyl methacrylate to fill the lumen of aspen (Feist et al. 1991).

Using ESCA to evaluate the oxidation of the surface after exposure to UV fluorescent lamps, Kiguchi (1992) reported a slight improvement in weather resistance for butylene oxide-treated Sugi (*Cryptomeria japonica* D. Don) compared with methylation of phenolic hydroxyls and acetylation. Kiguchi (1997) used ESCA to evaluate the UV resistance of Sugi modified with acetic anhydride and butylene oxide, and reported no improvement in the weatherability of the uncoated wood, but an improvement in the performance of transparent coatings applied over the modified wood. He noted a slight improvement in color retention for the modified wood.

Hon (1995) found that acetylation of southern pine gave only temporary improvement in color stability and, on the basis of ESR studies of a model compound [(4-methyl-2-methoxphenoxy)–hydroxypropiovanillone], suggested that the cleavage of the β-O-4 linkage in the model compound and the acetyl group formed phenoxy radicals. Hon attributed the formation of chromophoric groups to these phenoxy radicals.

Denes and Young (1999) incorporated various combinations of zinc oxide, graphite, benzotriazole, 2-hydroxybenzophenone, and phthalocyanine into polydemethylsiloxane, coated wood with these mixtures, and modified the wood surface using oxygen plasma. Following two weeks of artificial weathering (filtered xenon arc, water spray), some of the modified woods had decreased weight loss compared with untreated controls.

Hill et al. (2001) investigated chemical modification and polymeric grafting of methacrylic anhydride/styrene to Scots pine, and exposed the specimens to UV radiation and water using QUV artificial weathering apparatus (Q-Panel Co). They reported no positive effect for the treatment.

Imamura (1993) exposed acetylated wood (weight gains up to 20%) to natural weathering. SEM observation of the treated and untreated controls showed that both the acetylated wood and the controls degraded at the middle lamella, had enlarged bordered pits, and displayed checking along the microfibril angle of the S_2 layer of the cell wall, but the checking was less severe in the treated wood. The treated wood tended to hold the degraded fibers in place longer. Kalnins (1984) also reported no improvement in weather resistance for acetylated, methylated, or phenylhydrazine-modified wood. Ohkoshi et al. (1996) reported that acetylation combined with polyethylene glycol methacrylate treatment of wood prior to clear-coating improved the coating performance (decreased color change, peeling, and checking). Onoda (1989) modified buna (*Fagus crenata* Blume), sawara (*Chamaecyparis pisifera* Endl), and hinoki (*Chamaecyparis obtusa* Endl) with alkyl ketene dimers; the treatment caused wood degradation, but the treated wood was more resistant to weathering than the untreated ones. Pandey and Pitman (2002) reported improved weathering resistance of acetylated rubberwood.

Chang and Chang (2001) modified China fir (*Cunninghamia lanceolata* var. *lanceolata*) with acetic anhydride, succinic anhydride, maleic anhydride, and phthalic anhydride and evaluated photodegradation (color change) following QUV irradiation (315–400 nm, with peak radiation at 351). Acetylation was most effective in decreasing color change and phthalic anhydride acted as a photosensitizer.

Kiguchi (1990) modified sugi surfaces by cyanoethylation, benzylation, or allylation. The modified surfaces did not improve weather resistance, but the benzylation and allylation as a modified surface gave improved performance of an acrylic-silicon coating. Murakami and Matsuda (1990) reported that phthalic anhydride- and epichlorohydrin-treated wood degraded less in accelerated weathering exposure. Benzoylation of wood to about 70% weight gain was found to decrease wood weathering and ESR spectroscopy showed that the treatment decreased the amount of free radicals during exposure to UV radiation (Evans et al. 2002).

Rapp and Peek (1999) treated Scots pine sapwood, Norway spruce (*Picea abies* L.), English oak heartwood (Quercus robur L.), and Douglas-fir heartwood with varnish or melamine resin and exposed them outdoors for two years. Compared with untreated controls, the melamine resin provided protection against weathering, but not against checking or absorption of moisture.

Sudiyani et al. (1996, 1999a, 2002) treated albizzia (*Paraserianthes falcata* Becker) and sugi (*Cryptomeria japonica* D.Don) with acetic anhydride (AA), propylene oxide, paraformaldehyde, dimethyrol dihydroxy ethylene urea (DMDHEU), and phenol-formaldehyde (PF) resins and evaluated their weathering following one year outdoors in the tropics or 1080 hours of carbon arc (with water spray). They reported the best improvement for PF-modified wood, followed by AA-modified wood. The outdoor exposure was much more severe. They attributed the more severe weathering to high rainfall and possible decay in the tropical exposure.

It seems that cell wall modification such as acetylation, benzylation, etc., and lumen filling with methyl methacrylate give only modest protection against UV degradation.

7.5.7 Water-Repellent Preservatives

Water repellents give slight protection during early stage of weathering by decreasing the amount of degradation products washed from the surface (Feist 1987, Minemura et al. 1983). Wang and Tsai (1988) reported a decrease in weathering rate because of the water repellent. However, it was also reported that water repellent effectiveness is lost as wood weathers, and reapplications of the water repellent do not perform as well on weathered wood as on wood that has not previously been weathered (Voulgaridis and Banks 1981). The weathered substrate doesn't give a firm base for the water repellent to be effective.

7.5.8 Paints and Stains

Weathering of wood gives a surface that cannot hold paint very well, but the weathered surface can accept penetrating stains extremely well. Although the stains will not peel as does paint from weathered wood, the increase in the amount of stain does not improve the service life. (Arnold et al. 1992) A tape-peel test was used to determine adhesion of acrylic latex and an oil-modified acrylic latex primers to radiata pine exposed outdoors for five to ten days. (Evans et al. 1996) They found that the oil-modified acrylic latex bonded well, whereas the unmodified primer did not. Williams et al. (1999) reported more than 15 years of service life for oil-modified latex paint applied to severely weathered western redcedar and redwood. In this case the oil in the coating stabilized the surface, thereby improving the paint adhesion.

Semitransparent stain on southern pine pressure treated with chromated copper arsenate (CCA) had a longer service life than similar wood treated with brush-applied chromic acid prior to staining. (Feist and Williams 1991) The higher penetration and retention of chromium in the pressure-treated wood gave better protection. Plackett and Cronshaw (1992) reported similar results for artificial weathering of western redcedar and radiata pine pressure treated with various concentrations of CCA and brush-applied chromic acid prior to application of a clear moisture-curing urethane.

Performance of clear films on wood depends primarily on the weathering of the wood at the coating wood interface (Black and Mraz 1974, Feist 1979, Feist and Hon 1984, Williams 1983, Nakano et al. 1980; Lindberg 1986). Unless a coating has a pigment or other suitable additive to either absorb, quench, or block UV radiation, the radiation is absorbed by the wood surface at the

coating/wood interface. The wood degrades and the coating debonds. MacLeod et al. (1995) measured the interface degradation of western redcedar coated with a clear acrylic periodically as it weathered outdoors for 50 weeks using ATR FTIR. Cut-off filters (320, 360, 390, 490, and 620 nm) were used to evaluate the degradation at various wavelengths. They reported that lignin degradation at interface increased with decreasing wavelength.

Turkulin et al. (1997) exposed finished and unfinished Scots pine and Norway spruce to natural and QUV weathering. Finishes included both film-forming paints and semitransparent stains. On the basis of detailed SEM evaluations and tensile tests of the finish/wood interface, they reported that pine and spruce have the same modes of failure, but spruce had somewhat less structural change; early evidence of degradation were checks in the aspirated bordered pits; as weathering progresses, tension test specimens showed a brittle failure mode; opaque paints fully protected the interface; and solvent-borne stains failed at the interface.

A properly applied paint system gives the greatest protection to a wood surface against UV radiation. The pigments in the paint block the UV radiation, and the paint film retards water absorption. In the absence of a proper paint film, modification of wood with chromium compounds still stands out as the best treatment to retard photodegradation. Unfortunately, they probably will never be used as a commercial wood treatment because of environmental and health concerns. Chemical modification with organic compounds such as acetic anhydride, epoxides, grafted UV stabilizers, and methyl methylacrylate have shown only moderate efficacy. There is considerable research underway to develop new stabilizers, such as HALS, that can be grafted to wood to give a UV-resistant surface. Use of this technique along with UV absorbers in clear coatings will likely give UV-resistant wood/coating systems.

7.6 SUMMARY AND FUTURE CONSIDERATIONS

The middle lamella between the wood cells has a higher lignin content than the cell wall and degrades faster than the cell wall. The α-carbonyl sites in the lignin have been shown to be quite labile to absorption of UV radiation. ESR analysis confirms the formation of free radicals that initiate a series of oxidative degradation reaction. The cross-link density of lignin decreases, resulting in loss of lignin. Water plays a crucial role in washing the degradation products from the surface, leaching hemicelluloses, abrading the surface, and causing checking.

Much of the early research was done using UV radiation below 300 nm, but it showed, in a qualitative way, the depth of penetration of UV radiation, formation of free radicals, the importance of oxygen, and the reaction products. In many of the studies of photodegradation of wood, the UV radiation sources have not simulated the natural UV radiation. In addition, the sources covered extremely broad ranges. As was shown in Table 7.4, specific wavelengths of radiation can cause specific bond dissociation. To gain a better understanding of these reactions, filters should be used to study the chemical changes that occur at narrow wavelength ranges. This is the approach being used to study coating degradation by J. Martin and others at the National Institute of Standards and Technology. (Martin and Bauer 2002, Bauer and Martin 1999) By using narrow ranges of UV radiation, the chemistry specific to that wavelength can be studied. By using this approach, it might be possible to resolve the broad carbonyl absorptions that are observed in FTIR spectra of wood surfaces following photodegradation. By measuring the chemical changes at specific wavelengths, it might be possible to gain a better understanding of the mechanism of wood weathering.

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