WEATHERING OF WOOD

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Summary
What is the weathering of wood and why is it important? What factors are responsible for the weathering of wood and how do they affect the properties of wood? What are the best methods for protecting wood from the deleterious effects of weathering and why is the weathering of wood likely to remain an important subject for research in the future. This paper provides answers to all of these questions drawing upon the authors own research and the accumulated literature on the subject that dates back to the early 19th century.

1. Introduction

The surface degradation that occurs when wood is used outdoors and above ground is termed weathering. Weathering should not be confused with decay caused by basidiomycete fungi, which can rapidly reduce the strength of structural timber (Feist 1990). Because weathering is a superficial phenomenon its effects on the mechanical properties of wood are usually small and, accordingly, there are examples of wooden buildings such as the stave (pole) churches in Norway that are still structurally sound despite having been exposed to the weather for over 1000 years (Aune *et al.* 1983). The most obvious features of weathered wood are its grey colouration and rough surface texture (Fig. 1).

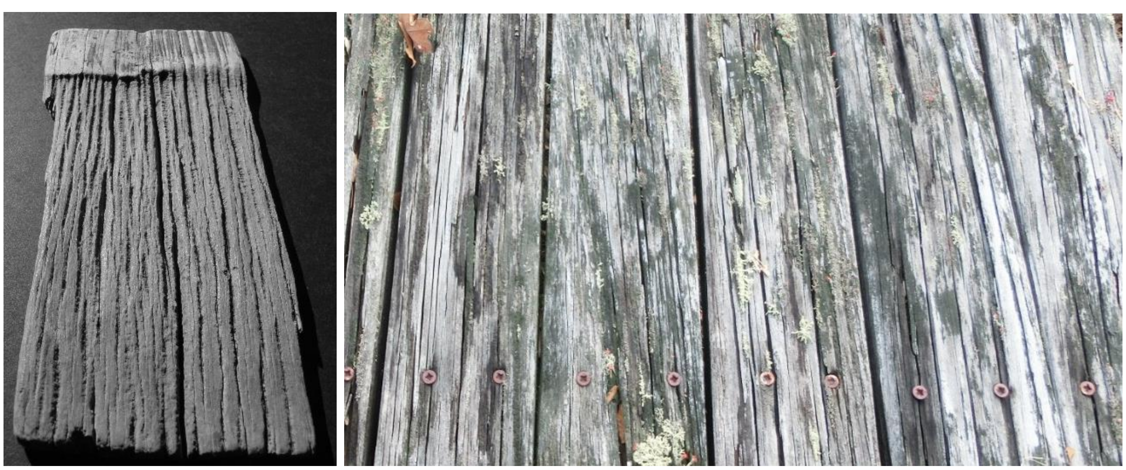

Figure 1: Weathered Norfolk Island pine (*Araucaria heterophylla* (Salisb.) Franco) roofing shingle, measuring 160 x 70 mm, from a 19th century building in Norfolk Island, Australia. Note the severe checking and erosion of the exposed surface (left); Treated southern pine (*Pinus* sp.) decking showing greying and checking of wood and colonization of the weathered surface by lichens (right)

Microorganisms colonize weathered wood, but conditions at exposed wood surfaces generally do not favour decay. Hence, the defining features of weathering are its superficial nature and the reduced role of microorganisms compared to environmental factors in degradative processes. In this paper I provide an overview of the weathering of wood, with emphasis on the causal agents of weathering, the important effects of weathering on wood properties and performance, and the protection of wood from weathering. I conclude the paper with a short section describing why research on the weathering of wood is likely to remain important in future. Readers requiring more comprehensive descriptions of the weathering of wood should consult the extensive reviews on the subject by Feist and Hon (1984), Feist (1990), Williams (2005), Evans (2009, 2013).

2. Importance of Weathering

Processing technologies and applications of wood that depend on its surface properties are severely affected by weathering. The poor performance of transparent coatings on wood is due in part to photodegradation of wood beneath the coating (Fig. 2). The photodegradation of wood before coatings are applied to wood also affects the performance of coatings (Desai 1967). For example, Evans *et al.* (1996) found that the adhesion of exterior acrylic primers on radiata pine (*Pinus radiata* D.Don) was reduced if the wood was exposed to the weather for only 5 to 10 days prior to painting. Because photodegradation is confined to wood surface layers, it does not greatly affect the mechanical properties of wood, but severe checking during weathering is associated with significant losses in the strength of wooden railway ties (Davis and Chow 1989). Weathering also reduces the natural durability of western red cedar (*Thuja plicata* Donn ex D.Don) shingles by leaching fungitoxic thujaplicins from wood (Schmidt and French 1976). There are reports of imperfect hardening of cement in contact with weathered plywood shuttering (form-ply). It was suggested that the presence of sugars at the surface of the weathered plywood, which were produced by the photodegradation of cellulose and hemicelluloses, interfered with the curing of the cement (Yoshimoto *et al.* 1967).

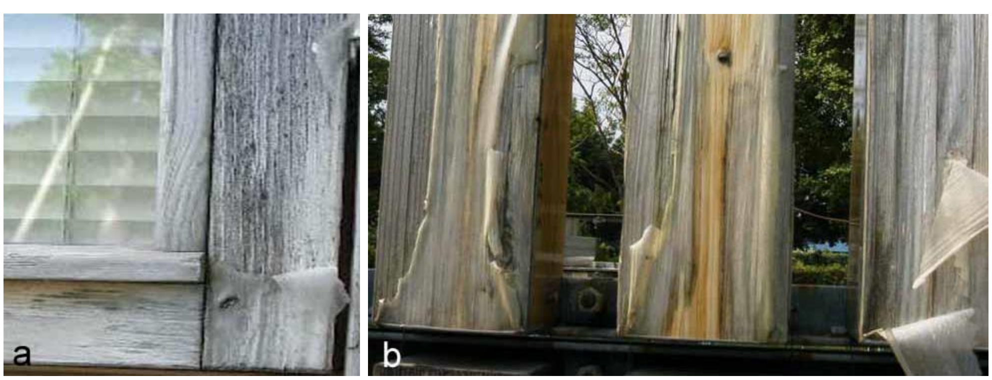

Figure 2: Peeling and delamination of clear coatings on wood due to photodegradation of wood beneath the coating: (a) Clear coating peeling from a vertical window casing in a private house in southern France. Note the fungal staining of wood beneath the clear coating; (b) Fluorine resin clear coating peeling from glulam test specimens exposed to the weather in Japan

3. Mechanisms and Environment

The main environmental factors that cause weathering are: solar radiation (ultraviolet and visible light), oxygen, water, heat, particulate matter, environmental pollutants and staining fungi. The maximum amount of solar radiation available at the earth's surface on a clear day is normally 1000 W/m^2. The composition of such radiation is approximately 5% ultraviolet (286-380 nm), 45% visible (380-760 nm) and 55% infrared (760-3000 nm). In order to act upon wood, solar radiation must be absorbed by one of wood's chemical constituents. Experimentation has shown that the aromatic lignin component of wood strongly absorbs ultraviolet (UV) light with a distinct maximum at 280 nm and a tail extending beyond 380 nm into the visible portion of the spectrum (Kalnins 1966). The heartwood of many wood species also absorbs light beyond 500 nm because of the presence of low molecular weight extractives such as flavonoids, tannins, stilbenes and quinones. In the case of synthetic homopolymers, photodegradation can be represented in a simplified manner as follows. Energy from absorbed radiation (*) can be dissipated in the polymer through the cleavage of molecular bonds (photolysis) resulting in the formation of a free radical ($R^* \rightarrow R\bullet$); that is a molecule which is highly reactive because it has an unpaired valence electron. Once a free radical has formed it can readily react with atmospheric oxygen to form a peroxy radical ($R\bullet + O_2 \rightarrow ROO\bullet$). The peroxy radical is capable of attacking the polymer backbone (RH) via hydrogen abstraction, forming a hydroperoxide and another free radical ($ROO\bullet + RH \rightarrow ROOH + R\bullet$). The hydroperoxide is very unstable to UV radiation and undergoes photolysis forming additional free radicals ($ROOH \rightarrow RO\bullet + \bullet OH$). The increasing accumulation of free radicals results in extensive cleavage of molecular bonds and consequent loss of the physical properties of the polymer. The photodegradation of wood proceeds in an analogous manner except that its degradation is more complicated because it consists of a blend of polymers (lignin, cellulose and hemicellulose) and low molecular weight extractives that differ in their susceptibility to solar radiation. Furthermore, the precise mechanisms and reaction pathways involved in the photodegradation of each of these components have yet to be elucidated. However, it is clear that the key step involved in the photodegradation of wood is photolysis and fragmentation of lignin resulting in the formation of free radicals (Feist and Hon 1984). These free radicals may then cause further degradation of lignin and photooxidation of cellulose and hemicellulose. Free radical reactions may be terminated by reaction of radicals with photodegraded lignin fragments forming coloured unsaturated carbonyl compounds, which explains why wood yellows when exposed to light. In accord with energetic considerations, the UV portion of the solar spectrum is most effective in causing degradation of wood, but wood exposed to visible light degrades at about half the rate of material exposed to the full solar spectrum

(Derbyshire and Miller 1981). The component of visible light that has sufficient energy to photodegrade lignin in wood is violet light, (380-430 nm, Kataoka *et al.* 2007).

Water has an important role in the weathering of wood. Dimensional change caused by the wetting and drying of wood generates surface stresses that cause checking and warping of timber (Feist 1990). Water leaches photodegraded lignin and hemicellulose fragments from weathered wood surfaces and is able to hydrolyze hemicelluloses. The photodegradation of wood is greater in the presence of moisture than under dry conditions (Turkulin *et al.* 2004), possibly because water molecules swell wood thereby opening up inaccessible regions of the cell wall to degradation (Feist and Hon 1984).

Heat accelerates the chemical reactions involved in the weathering of wood. Exposure of wood to low temperatures and repeated freezing and thawing can also contribute to the checking of wood. An additional factor involved in the weathering of wood in cold climates is abrasion by wind-blown particles of ice. For example, the Australian Antarctic explorer, Mawson (1915 pp. 123-124) wrote: 'the abrasion-effects produced by the impact of the snow particles were astonishing… A deal (*Pinus* sp.) box, facing the wind, lost all its painted bands and in a fortnight was handsomely marked; the hard knotty fibres being only slightly attacked, whilst the softer, pithy laminae were corroded to a depth of one-eighth of an inch' (approximately 3 mm). Windblown sand and salt can also cause similar, if less spectacular, abrasion of wood (Feist 1990).

The main pollutants in the atmosphere are dust and smoke particles and volatile pollutants including sulfur compounds, ammonia, nitrogen oxides, carbon monoxide and saturated and unsaturated aliphatic and aromatic hydrocarbons and their derivatives. There have been few studies of the effects of these pollutants on the weathering of wood, but observations in the field and *in-vitro* experiments all suggest that the weathering of wood is more rapid in polluted than in unpolluted atmospheres (Williams 1987).

A wide range of microorganisms including fungi, bacteria, algae and lichens colonize weathered wood surfaces. The fungus *Aureobasidium pullulans* (de Bary) G. Arnaud and other melanized fungi commonly colonize weathered wood surfaces and are responsible for the grey colour of weathered wood. *A. pullulans* is capable of withstanding temperatures of 80^{o}C and exposure to UV radiation. It also grows over a pH range of 1.9 to 10.1 and can survive for long periods without moisture. Hence, it is particularly well suited to the micro-environment of weathered wood, unlike the fungi that cause decay of wood (Schmidt and French 1976). Weathered wood is often visited by paper wasps (Polistinae), yellow jackets and hornets (Vespinae) that mine weathered wood surfaces to obtain delignified wood fragments, which they use to construct their elaborate paper-like nests (Fig. 3). Wood attacked by these insects has a stripy surface caused by the removal of strips of weathered wood, and the resulting contrast in colour between grey weathered wood and the underlying unweathered wood (Fig. 3)

Figure 3: A wasp (*Vespula vulgaris* L.) removing weathered wood from a weathered wood surface (left); paper-like wasp nest constructed from weathered wood (centre); Stripy appearance of weathered wood attacked by wasps (right)

4. Effects of Weathering

Wood exposed to the weather changes colour very rapidly. Light coloured woods, including most coniferous species, initially darken in colour and become yellow or brown due to the accumulation of photodegraded lignin compounds in the wood. Dark coloured woods that are rich in phenolic extractives may fade initially before becoming yellow or brown (Feist 1990). Irrespective of these initial colour changes, wood exposed outdoors for 6 to 12 months (depending on climatic conditions) becomes grey due to the colonization of photodegraded, cellulose-rich, surface layers by dark coloured staining fungi. Wood exposed outdoors in coastal (exposed to salt) or very dry environments where microbial activity is restricted is often an attractive silvery-grey color.

The rapid erosion of low-density earlywood often gives weathered wood a corrugated appearance (Fig. 1). The rate of erosion of wood during exterior exposure is inversely proportional to density (Sell and Feist 1986). Accordingly, low density species such as western red cedar erode at a rate of 12 mm per century when exposed vertically facing south in the Northern Hemisphere, whereas comparable figures for higher density softwoods such as Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco.) and high density hardwoods are 6 mm and 3 mm, respectively (Feist 1990). In addition to erosion, the surface texture of weathered wood is further degraded by the formation of macroscopic checks. Photodegradation of wood and stresses generated by wetting and drying are responsible for the formation of such checks, which often develop where adjacent cells or tissues differ in cell wall thickness or strength. For example, checks often develop at growth ring boundaries and at the interfaces between rays and tracheids. Microscopic changes to the structure of wood precede any evidence of macroscopic damage during weathering. The lignin rich middle lamella that bonds adjacent tracheids and fibres together is rapidly eroded during weathering, and adjacent primary and secondary cell wall layers show progressive thinning with increasing exposure (Fig. 4a-d). The most obvious changes to the microscopic structure of longitudinal surfaces are the formation of microchecks originating in bordered and half-bordered pits and the degradation of ray tissues (Fig. 4e-f). Microchecks and the voids at wood surfaces created by degradation of rays are often colonized by staining fungi (Fig. 4e-f).

All of the major chemical constituents of wood are degraded during weathering. Lignin is depolymerized and, as mentioned above, low molecular weight lignin fragments are leached from wood by rain. The use of spectroscopic techniques, such as Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy, that can probe the chemical composition of surfaces has shown that the degradation of lignin at exposed wood surfaces is extremely rapid. For example, FTIR spectroscopy of weathered radiata pine veneers showed a remarkably rapid decrease in the peak at 1505 cm^{-1}, which corresponds to aromatic C=C bond stretching in lignin. Spectra suggested perceptible surface (1-2 μm) delignification after 4 hours exposure, substantial delignification after 3 days and almost complete surface delignification after 6 days (Fig. 5) (Evans *et al.* 1996). Hemicelluloses, particularly those containing xylose and arabinose, are also degraded and leached from weathered wood, and hence, as mentioned above, weathered wood surfaces are rich in cellulose. Because of this it was assumed for many years that cellulose was less affected by weathering than the other chemical constituents of wood, but viscometry studies of cellulose isolated from weathered wood have shown that cellulose in wood is rapidly depolymerized when exposed to the weather (Derbyshire and Miller 1981, Evans *et al.* 1996).

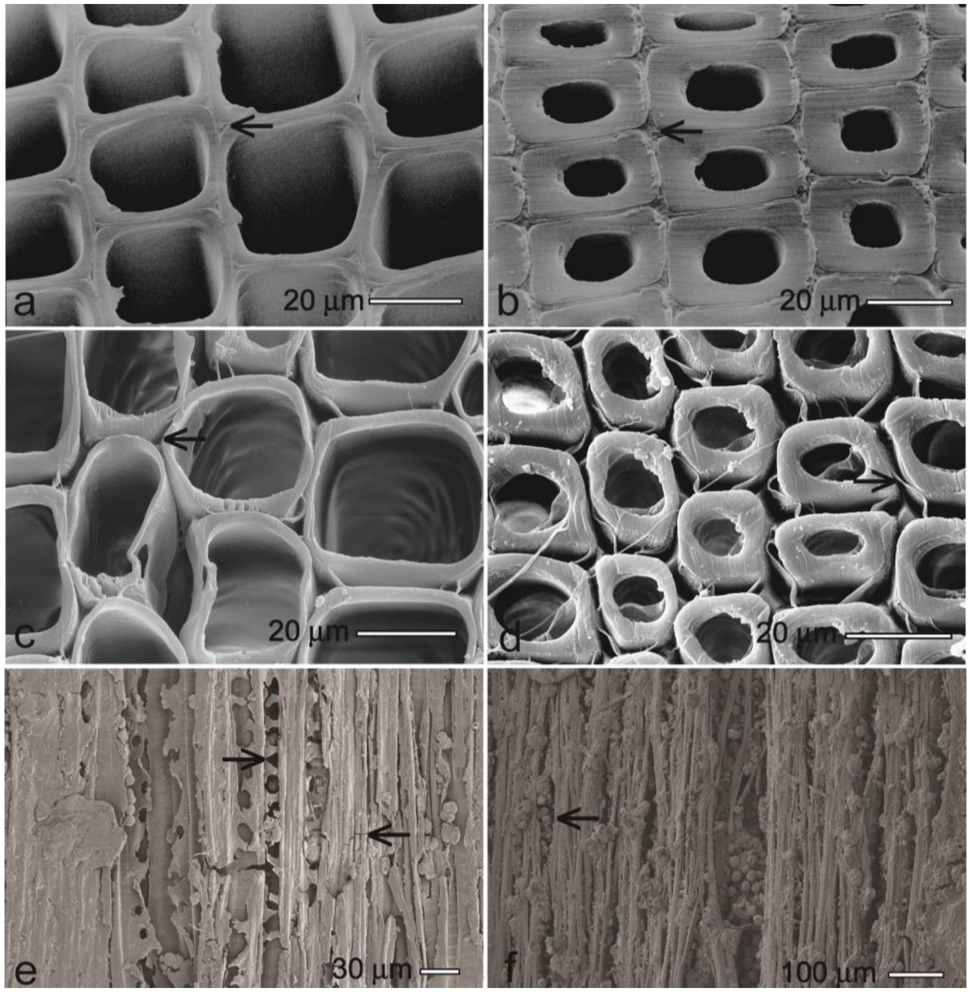

Figure 4: Effects of weathering on the microscopic structure of wood surfaces: (a) Unexposed Scots pine (*Pinus sylvestris* L.) earlywood tracheids with thin undamaged cell walls and large cell lumens. Note the lignin-rich middle lamella that cements tracheids together, (arrowed); (b) Unexposed Scots pine latewood tracheids with thick cell walls and small lumens. Note the middle lamella, (arrowed); (c) Scots pine earlywood tracheids exposed to the weather for 30 days. Note erosion of middle lamellae, particularly at cell corners and thinning of cell walls, (arrowed); (d) Scots pine latewood tracheids exposed to the weather for 30 days. Note erosion of middle lamellae and delamination of cell walls, (arrowed); (e) Radial longitudinal Douglas fir surface exposed to the weather for 415 days. Note micro-cracking of bordered pits in earlywood (arrowed center), fracture of latewood tracheids, (arrowed right) and colonization of voids by staining fungi; (f) Tangential longitudinal surface of the tropical hardwood, ipe (*Tabebuia* spp.), exposed to the weather for 1 year. Note separation of fibres at surface, voids created by degradation of rays (arrowed left) and extensive colonization of surface by staining fungi

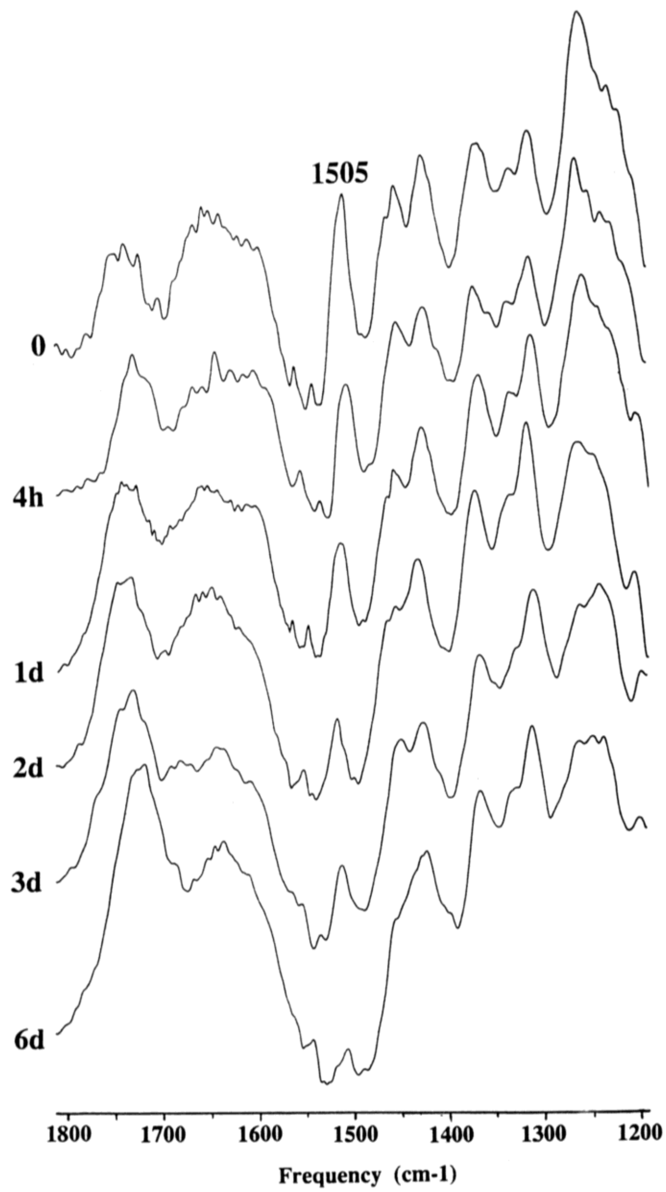

Figure 5: Fourier transform infrared internal reflectance spectra of radiata pine veneers exposed to the weather for periods ranging from four hours (4h) to six days (6d) compared to the spectrum for an unexposed control (0)

5. Protection

The most common method of protecting wood from weathering is through the use of coatings. Paints contain pigments that screen wood from solar radiation and because they form a film over the wood surface they prevent surface wetting and erosion. A correctly applied and maintained paint system including a primer and at least two topcoats can greatly reduce the deleterious effects of weathering on wood (Feist 1990). However, paints are less effective at controlling decay and dimensional movement and therefore they often perform better on wood that has been pre-treated with a water-repellent preservative. Paints obscure wood's natural appearance and texture, and their tendency to trap water and encourage decay has led to increased use of penetrating water repellent stains as a means of protecting wood used outdoors. Stains contain a variety of additives to reduce the weathering of wood, including pigments and UV stabilizers to screen wood from solar radiation, hydrophobic additives to repel water and reduce checking, and a biocide to control the growth of microorganisms. Stains provide protection against weathering for 2-5 years depending on wood species and surface texture, type and quantity of stain applied to the wood and degree of exposure to the weather. Paints and to a lesser extent stains modify the appearance of wood. For end uses where it is important to retain the woods natural colour or texture the wood can be finished with a clear coating. Clear coatings, however, although they often contain UV stabilizers and a biocide, are limited in their ability to protect wood from weathering because they transmit light, which can degrade the underlying wood surface. Hence, clear coatings such as varnish perform badly on wood used outdoors and invariably fail by peeling and cracking within 6 months to 2 years of application. One means of increasing the performance of clear finishes on wood is to photostabilize the underlying wood surface prior to application of the clear finish. Pre-treatment of wood with dilute aqueous solutions of transition metal compounds (Cr, Mn, Ti, Cu), and particularly chromium trioxide can photostabilize wood and increase the longevity of clear coatings applied subsequently to the wood. When wood is treated with chromium trioxide, lignin phenolic sub-units at wood surfaces are modified producing oxidized lignin complexes with considerable light, thermal and solvolytic stability (Schmalzl *et al.* 2003). It has been suggested that such complexes could function as 'an ultraviolet screen' protecting wood from the effects of the weather. Health concerns about the use of hexavalent chromium, however, have discouraged commercial development of this concept and until effective methods of photostabilising wood are developed it is unlikely that clear finishes on wood will be able to match the exterior performance of paints and other highly pigmented finishes.

Chromium-containing wood preservatives such as chromated-copper-arsenate are also able to photostabilize wood surfaces, and when they contain wax or oil they also reduce the surface checking of wood exposed to the weather (Christy *et al.* 2005). Wax and oil emulsion additives are also added to metal-free preservatives to reduce the swelling and checking of wood used outdoors. The swelling of wood can be reduced by treatments that chemically or thermally modify wood's molecular structure to reduce its affinity to water. Treatments that fall in to this category include acetylation, thermal modification and the impregnation of wood with resins. These treatments, which have all been commercialized, reduce the checking of wood exposed to the weather, but they retard rather than block surface photodegradation of wood. Chemical bonding or grafting of UV absorbers to wood is more effective at photostabilising wood, but commercialization of such protective treatments awaits the development of less costly UV absorbers that can be more easily bonded to wood (Kiguchi and Evans 1998).

Despite the desire to protect wood from weathering, in certain applications weathered wood is preferred to fresh wood. A good example of this is the use of weatherboards for the construction of "New England" type barns, where the wood may be treated prior to building construction to give the building an aged appearance in keeping with its rural surroundings (Anon 1976). The treatments involve physical distressing (rough sawing, sand-blasting, wire-brushing, and planning with notched knives) to give the surface the texture of weathered wood (Anon 1976), followed by chemical treatment to impart a grey colour to the wood. Various chemicals have been used for the latter purpose including bleaches, or tannins in combination with ferrous ammonium sulphate (Cassens and Feist 1991). Alternatively, a grey stain can be applied to wood which is "durable enough to allow a soft transition between its own degradation and the eventual development of the grey colour produced by natural weathering when the wood is exposed outdoors" (Podgorski *et al.* 2009).

6. Future Directions

Architects and engineers are increasingly insisting on materials that offer longer service life and lower repair and maintenance costs. In addition there is strong pressure to use materials that can be easily recycled and produced on a sustainable basis. Wood is a renewable material that can be easily repaired and in most cases recycled. However, weathering reduces the service life of wood and increases its maintenance costs. For example, premature failure and replacement of preservative-treated decking is often caused by checking (McQueen and Stevens 1998), and the higher maintenance costs of exterior wooden joinery compared to substitutes made from unplasticized polyvinyl chloride or aluminum are caused in part by weathering-induced failure of surface coatings. Hence, there is likely to be continuing interest in the development of additives and treatments to reduce the weathering of wood. A deeper understanding of the mechanisms involved in photodegradation of wood could lead to more economical and effective methods of photostabilizing wood, which could significantly improve the durability of clear finishes for timber. Wood is increasingly being converted into a wide range of composites and being combined with a diverse range of other materials including thermoplastic and thermosetting polymers, ceramics and other lignocellulosics. The evaluation of the weathering resistance of such materials and the development of appropriate treatments to enhance their durability will become increasingly important in future.

7. Literature

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