Study on Weathering Behavior and Feasible Weatherproof Treatments of Cunninghamia lanceolata (Lamb.) Hook. under Natural Conditions

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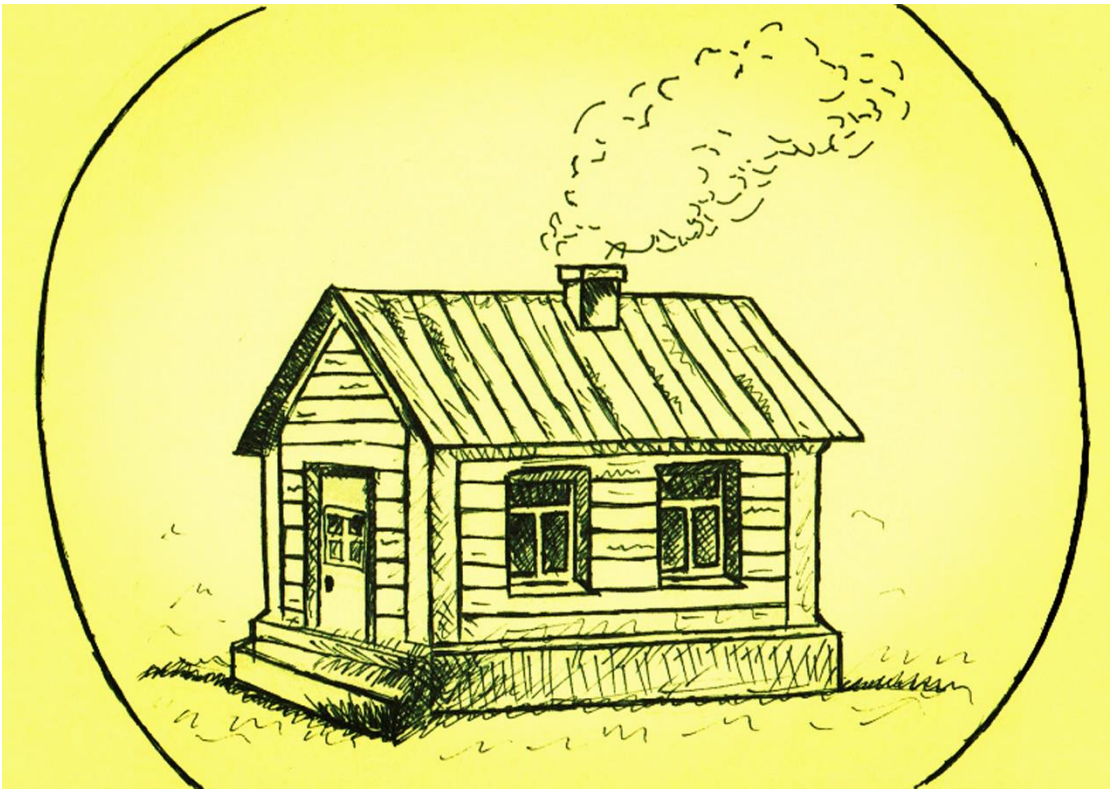
CHAPTER 1 General Introduction



1.1 Species introduction

Cunninghamia lanceolata (Lamb.) Hook. (Chinese fir) is a member of the family Cupressaceae. It is an evergreen tree that can grow up to 50 m in height and more than 3 m in diameter. It grows naturally in China, Laos, Vietnam, Malaysia, and Cambodia and plantations have been established in other countries, including Argentina, Japan, New Zealand, and South Africa (Figure 1.1). *C. lanceolata* forms mixed broad-leaved forests or small, pure stands on rocky hillsides and roadsides, at altitudes ranging from 200 to 2800 m (Fu et al. 1999, Orwa et al. 2009). The natural distribution area of *C. lanceolata* is a subtropical humid climate, warm and humid, with abundant rainfall (Wu 1984). *C. lanceolata* adapts to the climatic conditions with an annual average temperature of 16℃–19 ℃, extreme minimum temperature of −15 ℃, and annual precipitation of 900–2350 mm (Wu and Hou 1995, Jøker 2000, Orwa et al. 2009).

C. lanceolata is an important native tree species that has been widely planted in mountainous areas in the tropics and subtropics in China for more than 1,000 years. It grows rapidly and has been used for a variety of wood products (Li et al. 1999). Its advantages are excellent material properties, aroma, moderate hardness, straight texture, and easy processing (Deng 2007). The seeds contain approximately 20% oil and are used to make soap. The heartwood and branches, roots, bark, leaves, seeds, and oil of *C. lanceolata* can be used for medicine (Ye et al. 2005, Zhang et al. 2011). The timber of this species is strongly resistant to rotting and it is not eaten by termites; thus, it has been widely used for constructing buildings, bridges, ships, and lamp posts in furniture manufacturing and for wood fiber (Fu et al. 1999, Jøker 2000, Orwa et al. 2009).

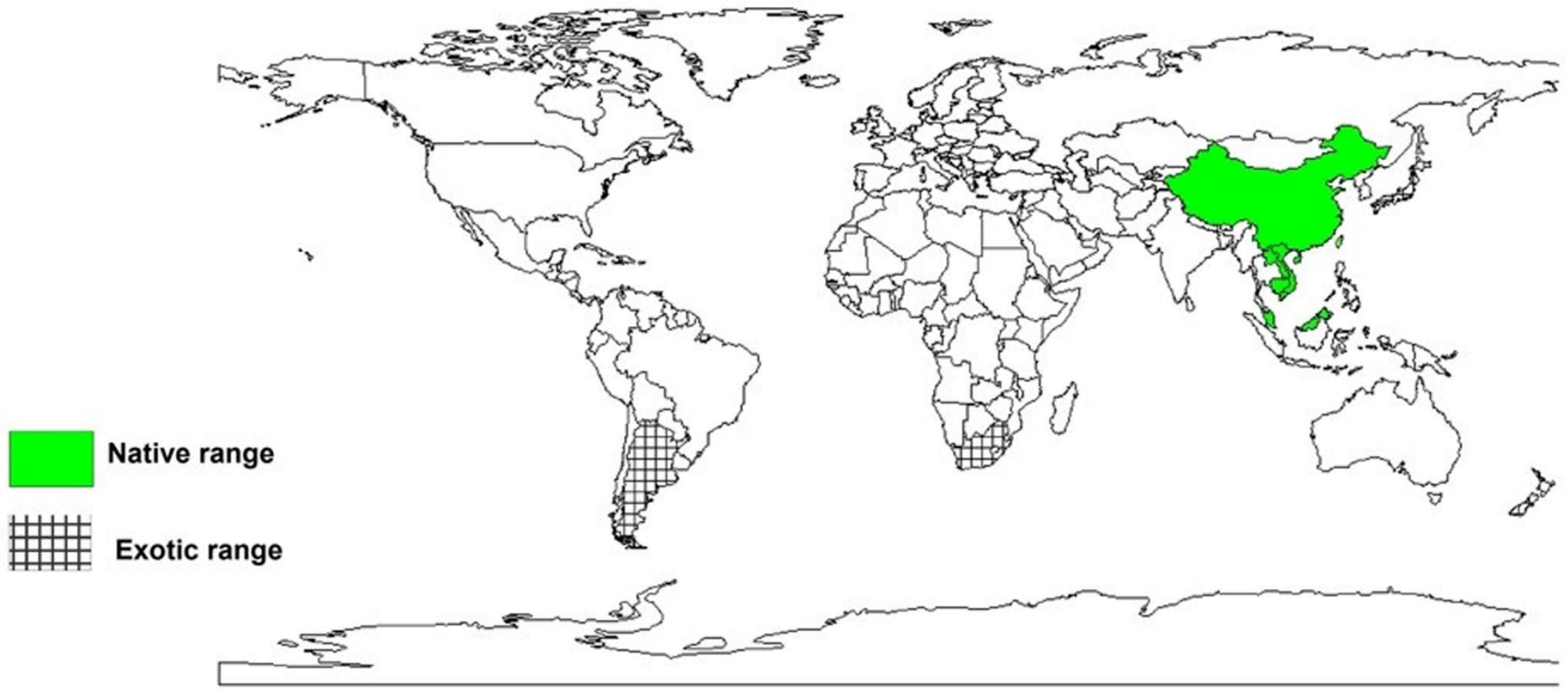


Figure 1.1 Distribution of *Cunninghamia lanceolata* (Lamb.) Hook (Chinese fir) in native countries and in countries where the species has been planted (adapted from Orwa et al. 2009).

1.2 Weatherability of wood

Exposed to the outdoor natural environment, wood is subjected to conditions including photodegradation by ultraviolet (UV) light, leaching by rain, hydrolysis, swelling and drying shrinkage, erosion by wind load, and corrosion by microorganisms (Feist and Hon 1984, and Feist 1990, Evans et al. 1993). Over time, weathering of wood surfaces can cause color, chemical, physical, mechanical, and microscopic changes (Roger et al. 2000). The resistance of wood to these effects and the changes in the properties of wood caused by these effects are called the weatherability of wood (or weathering resistance of wood) (Evans 2005, Williams 2005).

Due to the influence of outdoor factors, especially ultraviolet radiation and erosion caused by wind and rain, changes take place on the wood surface (Hon 1975, Hon and Chang 1984, Hon 1991, Evans et al. 2005). Because the wood surface is on the outside, it is susceptible to external interference, and it changes frequently with the climate (Derbyshire et al. 1981). Therefore, the microstructure of the cell wall changes on the wood surface. The effect of expansion and drying stress causes wood to become rough, cracked, and then warped (Mawson 1915, Borgin 1969, Evans et al. 1988, Evans and Banks 1988, 1990). Some chemical changes of the wood surface increase the color change of wood and soften its surface (Spedding 1970, Raczkowski 1980, Chang et al. 1982, Williams 1987, Hon and Feist 1993, Park et al. 1996).

The effective treatment of wood is an important way to improve its weathering resistance. The wood treatments can prolong the service life of wood products. In addition, it also can reduce the maintenance cost of the wood structure (Feist 1989). Extensive research has been conducted to improve the weatherability of wood. For example, acetylation, high temperature, and high humidity heat treatment are methods that can significantly improve the dimensional stability and color stability of wood (Kalnins 1984, Feist et al. 1987, Evans et al. 2000, Hill et al. 2001, Chang 2001a, Chang and Chang 2001b, 2006, Evans et al. 2005). The treatment of wood with resin / paraffin

water repellent can significantly reduce the flow of water inside the wood, improving the dimensional stability of wood in wet environments (Ashton 1967, Desai 1967, Borgin 1968, Boxall 1977, Underhaug et al. 1983, Williams et al. 1987, 1990, Feist 1988, 1989, Williams and Feist 1993a, 1993b, Kiguchi et al. 1996, 1997a, 1997b, Singh and Dawson 2003, Hansmann et al. 2005, Lesar et al. 2011). Different physical or chemical methods can be used to treat wood according to different causes of wood change.

C. lanceolata is extensively used in outdoor environments. For example, it has been used as the main building material of Chinese Dong minority drum towers and wind and rain bridges (Figure 1.2) (Cai et al. 2016, Luo et al. 2019). Wood quality is significantly affected during natural exposure (Williams 2005). Despite the numerous studies on the wood properties of *C. lanceolata*, there are still many unknowns regarding its weathering. Studying the weatherability of wood is important because it can aid in determining the most effective treatment methods and can guide the establishment and refinement of *C. lanceolata* weathering protection methods.

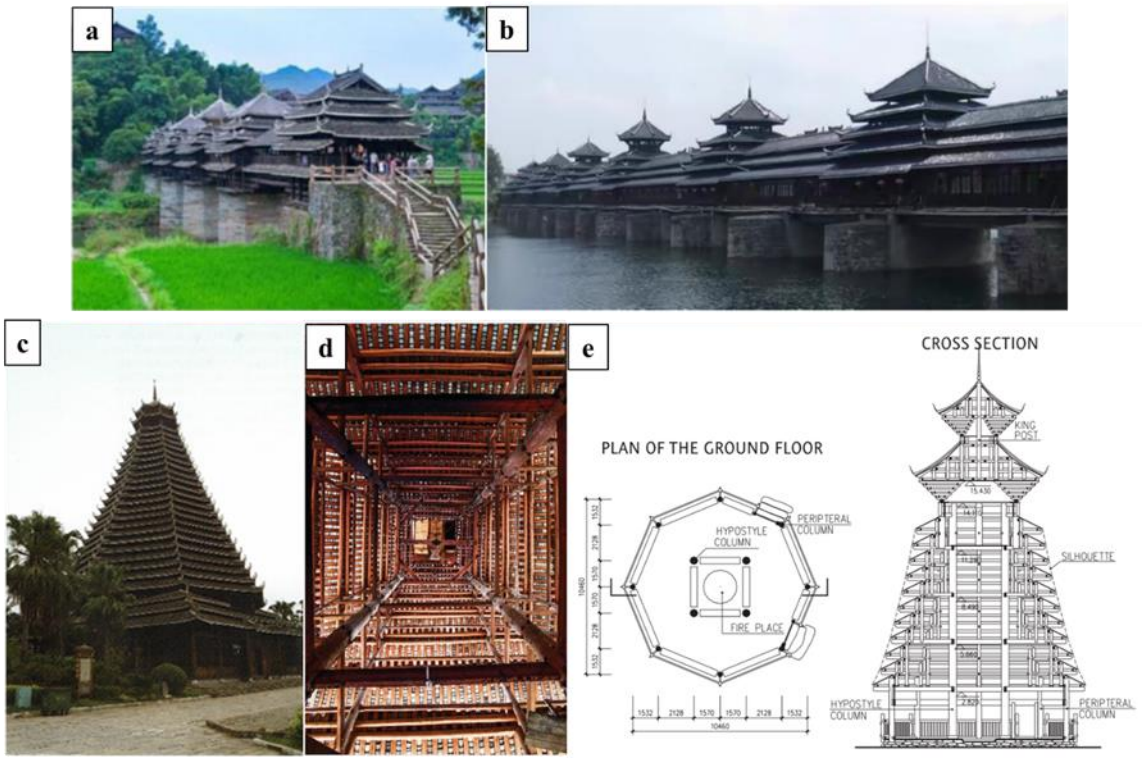


Figure 1.2 Ancient buildings constructed of *C. lanceolata*

(Luo et al. 2019, Cai et al. 2016).

a and b. Wind and rain bridge; **c, d and e.** Chinese Dong minority drum towers.

1.3 Study objectives

1.3.1 General objective

The purpose of this study is to clarify the weathering behavior and the effects of feasible weatherproof treatments on the weatherability of *C. lanceolata*. The results should provide relevant information to improve the weatherability of *C. lanceolata* in natural environments in order to establish and refine the anti-weathering pretreatment programmes for this species. The results should also provide references for prolonging the service life of wood products and for improving the utilization ratio of timber.

1.3.2 Specific objectives

I. To obtain information on degradation characteristics of *C. lanceolata*

II. To estimate the effect of heat-treated on weatherability of *C. lanceolata* under natural condition

III. To estimate the effectiveness of low-molecular weight phenolic resin for improving the durability of *C. lanceolata*

1.4 Thesis structure

The dissertation is divided in to six chapters. The scientific articles (two) of this dissertation have been published in international journal. The articles are reprinted in this dissertation as chapters with the permission of the publisher.

Chapter 2 – Literature review

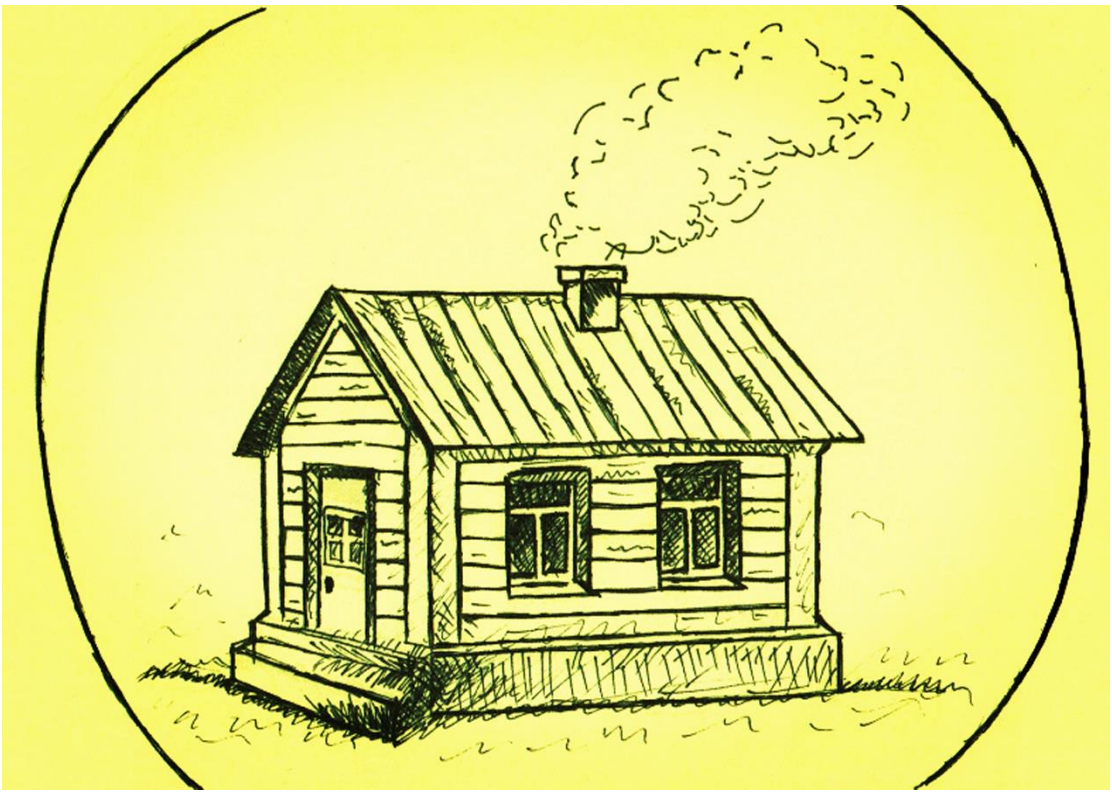
Chapter 3 - Cui X J. & Matsumura J. (2020). Weathering behavior of *Cunninghamia lanceolata* (Lamb.) Hook. Under natural conditions. *Forests*, 11, 1236; doi:10.3390/f11121326.

Chapter 4 - Cui X J. & Matsumura J. (2019). Wood surface changes of heat-treated *Cunninghamia lanceolata* following natural weathering. *Forests*, 10, 791; doi:10.3390/f10090791.

Chapter 5 - Effectiveness of low-molecular weight phenolic resin for improving the durability of *Cunninghamia lanceolata* (Lamb.) Hook.

Chapter 6 – General discussion, conclusion and Recommendations

CHAPTER 2 Literature Review



2.1 Introduction

This chapter provides an overview of weathering. Further, it summarizes the characteristics of wood weathering behavior. The effects of heat treatment on wood degradation characteristics are described, and resin impregnation, which is important for wood weathering resistance, is discussed. Finally, the development and use of wood weatherability are discussed.

2.2 Weathering behavior of wood

Wood is widely used as a raw material for construction and will deteriorate under continuous exposure to sunlight or outdoor conditions. In recent years, with the development of the wood products industry, the application of these materials in the outdoors has also significantly expanded. The study of protecting the wood appearance and preventing wood surface weathering has attention (Caba et al. 2007). Based on the understanding of wood weathering behavior, wood is expected to develop more effective protection systems to limit surface deterioration and protect wood structural properties (Evans 2008).

By investigating the weathering behavior of wood, it can be found that the weathering process of wood is the result of chemical, mechanical, and light energy factors. The effect of weathering is usually on the wood surface, about 2–3 mm deep. Weathering can significantly alter the appearance and surface properties of wood.

Chemical properties

The main chemical components of wood are degraded during weathering. UV light degrades wood, resulting in a decrease in the contents of wood methoxy and lignin, and an increase in the contents of acid and carbonyl (Leary 1967, 1968). Kalnins (1966) identified carbon monoxide, carbon dioxide, hydrogen, water, methanol, formaldehyde and organic acids as the degradation products of wood during weathering (Hon and Chang 1984).

Wood is a good light absorbing material. Lignin is the most sensitive component of wood to weathering. The different components of wood have different reaction groups and sites, such as hydroxyls, carboxyls, phenolics, and carbonyls. These groups can interact with ultraviolet light to generate free radicals, which absorb 80%–95% UV light. The destruction of polymers in wood is mainly caused by free radical reactions, which also lead to the degradation of lignin, showing a white to gray wood color (Hon and Ifju 1978; Brown and Simonson 1957). Thus, the change in wood color is the most direct index of chemical changes or biological destruction. Ultraviolet light also acts with moisture, heat, air pollutants and oxides (such as oxygen, lignin in wood cell walls and fiber) in the surrounding environment, resulting in the decomposition of lignin and cellulose in wood cell walls. The water in the surrounding environment will wash the degradation products out of the wood.

After absorbing ultraviolet energy, the lignin on the wood surface is decomposed first, followed by hemicellulose. Cellulose has higher molecular weight than hemicellulose and is protected by a crystal structure, so it decomposes last (Rowell 1983). Cellulose and hemicellulose in wood cell walls absorb only a small amount of light energy, but they are still decomposed by light. The relative molecular weight of hemicellulose is much lower than that of cellulose. When both of them experience the same amount of photolysis, the solubility of hemicellulose is much higher than that of cellulose because of the smaller relative molecular weight (Evans et al. 1992). The cellulose in the amorphous region of microfibrils is decomposed first, whereas the cellulose in the crystalline region is arranged closely and is thus the most stable.

Physical properties

Wood surface erosion due to weathering is a rather slow process. The extent of the wood surface erosion varies by tree species. The erosion rate of wood during external exposure largely depends on its density. A study of accelerated weathering showed that the wood density was inversely related to the erosion degree, but there was no linear relationship (Sell and Feist 1986) (Fig.2.1). For example, low-density species such as

western red cedar (*Thuja plicata* D. Don) are eroded at a rate of 12 mm per century. Hardwoods are generally denser than softwood, so they are more resistant to weathering. High-density hardwoods are eroded at a rate of 3 mm per century (Feist 1990). The erosion rate of earlywood is faster than that of latewood (Williams et al. 2001a, 2001b).

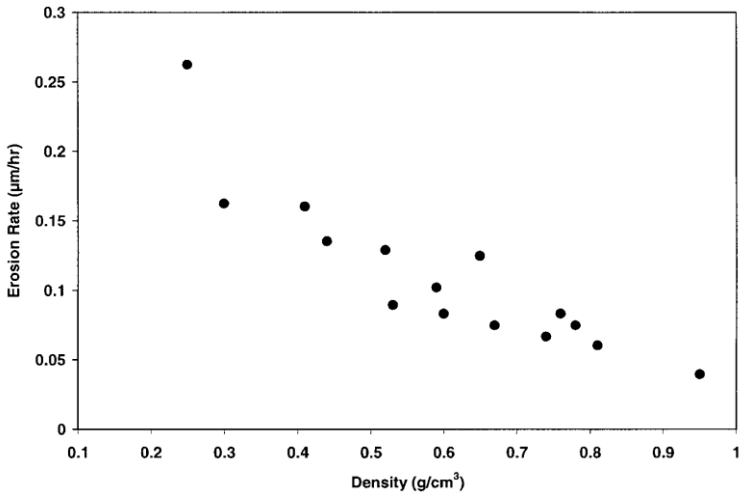


Figure 2.1 Erosion rate versus air dry wood density of a range of wood species subjected to artificial accelerated weathering (Sell and Feist 1986).

The presence of water will also lead to dry shrinkage and swelling of wood. Because the surface of wood is in direct contact with water and sunlight, the dry shrinkage and swelling caused by water is more frequent, which eventually leads to tensile stress on the wood surface. When the tensile stress exceeds the compressive strength of wood, the wood surface will crack (Evans 1989, Yata and Tamaru 1995).

Because the surface becomes rough, the gloss of wood decreases during weathering (Hon and Minemura 1991). Separation of wood fibers is a result of different stress of the wood surface (Panshin and DeZeeuw 1980). The rapid erosion of low-density wood often results in a corrugated appearance of weathered wood (Fig.2.2).

Figure 2.2 The corrugated appearance of wood after weathering.

The weathering behavior of various tree species is different (Hon and Feist 1986, Evans 1988, Anderson et al. 1991, Nzokou et al. 2011, Agnieszka 2013, Zborowska et al. 2014, Jankowska et al. 2014). According to the anisotropy of wood itself, the wood properties of different parts of the same tree species are different (Akachuku 1984, Watanabe et al. 1998, Ivkovi´c et al. 2009, Hasegawa et al. 2011, Borrega and Borrega 2015). Therefore, it is speculated that there are also differences in weathering behavior within wood. Natural weathering is usually a long-term research process. Various problems in the process of the experiment will directly affect the accuracy of the final experiment. Some experiments were carried out through artificial weathering experiments.

Artificial weathering tests are usually considered to simulate outdoor environments, but this method only includes ultraviolet radiation and water cycling. There are many other factors affecting the natural environment, such as microorganisms, air pollutants, and chemicals and biological agents (Williams 2005). Therefore, artificial weathering tests can not completely replace the study of the natural weathering of wood. It is still necessary to test the service life of wood under natural conditions (Williams 2005, Buchner et al. 2018). The study of natural weathering often requires a long-term process. In fact, the changes in surface weathering characteristics begin at

the time when wood is exposed to the outdoor environment. It is reported that the surface properties of wood can change significantly under short-term irradiation (Evans et al. 1996, Tolvaj et al. 2009). Therefore, paying attention to the change in the wood surface is a method to evaluate the short-term weatherability of wood.

2.2.1 Anatomical structure of wood

When wood is used outdoors, the cracking degree of the wood surface is aggravated by long-term exposure to sunlight, especially ultraviolet radiation. The degradation of lignin caused by light weakens the mechanical properties of wood cell walls, causing the small cracks formed by irradiation to deepen along the longitudinal direction and combine with other similar cracks to form visible large cracks. This indicates that there is a correlation between the microstructural changes of cells formed by lignin photodegradation and the large cracks in wood.

During weathering, damage to the wood microstructure usually precedes macroscopic damage. Microscopic examination is performed on the cell wall. The structural damage of wood due to weathering was studied by scanning electron microscopes (Borgin 1970, 1971, Borgin et al. 1975). These studies revealed the slow degradation and eventual destruction of the bond strength in the middle lamella, cell wall layers, and wood tissues. Tracheids may also separate as a result of erosion and checking of the middle lamella (Miniutti 1964,1967). During weathering, the lignin-rich middle lamella and primary cell walls are rapidly eroded, resulting in thinning of the cell walls with prolonged exposure time (Evans 1989, Evans et al. 2002) (Figure 2.3a–d). In the process of wood weathering, the middle lamella is completely destroyed, which causes the wood fibers to be washed away by rainwater (Borgin 1969). During weathering, significant changes occur in the position of bordered pits (Figure 2.3e–f). This characteristic first occurs in earlywood and then in latewood. As the exposure lengthens, the pits are destroyed until the boundary is reached (Miniutti 1964,1967). A similar decline occurs in the half-bordered pits, but their velocity is slower than that of the bordered pits (Miniutti 1967). Conversely, Chang et al. (1982) found that half-

bordered pits degraded at a faster rate than bordered pits in southern pine exposed to artificial UV light. Many studies have described the observation of the microscopic changes of the wood surface after artificial weathering (Miniutti 1967). In the study conducted by Feist and Hon (1984), the changes in the wood surface after accelerated artificial weathering were very similar to those caused by outdoor natural weathering.

In the process of wood weathering, the ray structure undergoes obvious changes. Conifer ray degradation occurs easily, but the degradation of wood rays containing extracts is prevented. In hardwoods such as beech, large multiseriate rays have been reported to be more resistant to weathering than the surrounding ground tissue (Kucˇera and Sell 1987). The first sign of deterioration of softwood surfaces is the enlargement of apertures of bordered pits in the radial walls of earlywood tracheids. Next, microcracks occur, which enlarge principally as a result of contraction in cell walls (Miniutti 1967,1970). A single fiber has good stability and durability. The most stable part of the whole fiber seems to be the microfibrils. Due to the loss of the bond structure between the primary microfibers and the loss of the adhesion ability between the layers, each layer of the cell wall is destroyed, and all pit sizes increase, resulting in the weakening of the whole fiber structure. The destructive weathering process is limited to 2-3 mm of the wood surface (Feist and Hon 1984).

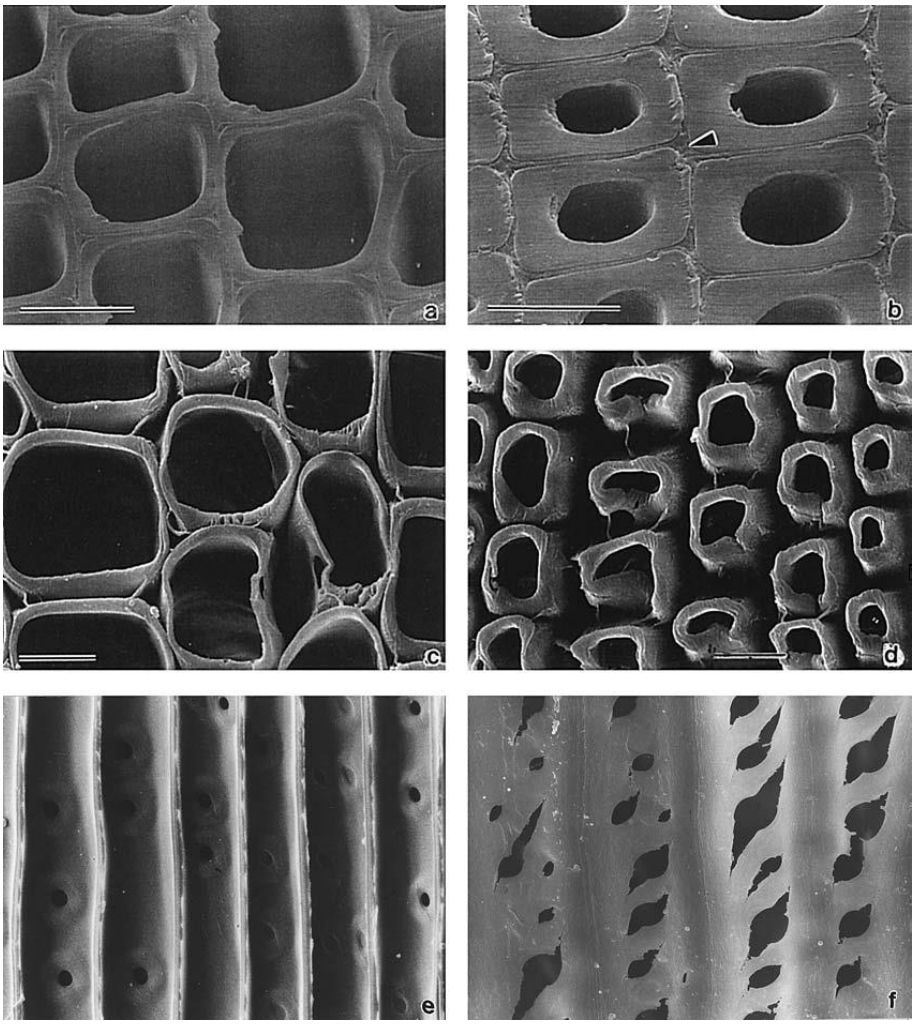


Figure 2.3 a–f Effects of weathering on the microscopic structure of Scots pine wood. (a) Unexposed earlywood tracheids with thin undamaged cell walls and large cell lumens; (b) Unexposed latewood tracheids with thick cell walls and small lumens (note the middle lamellae that cements tracheids together, arrowed); (c) Earlywood tracheids exposed to the weather for 30 days (note the erosion of the middle lamella, particularly in the cell corners and the thinning of cell walls; (d) Latewood tracheids exposed to the weather for 30 days (note erosion of the middle lamellae and delamination of cell walls); (e) Unexposed earlywood tracheids showing the apertures of bordered pits that allow water in conifer trees to flow from one cell to another; (f) Earlywood tracheids exposed to the weather for 30 days (note micro-checking originating in the bordered pit apertures). (Evans 1989, Evans et al. 2002, Miniutti 1964, 1967).

The deterioration of the wood surface during the natural weathering of samples is observed by SEM. This method is a valuable tool to observe the microanatomical details of degraded wood, including the cell wall shape, and to assess cell wall changes. It provides information on surface degradation. The surface degradation of exposed wood can be observed by low-vacuum scanning electron microscopy (LVSEM). The advantage of this method is to obtain information intuitively and accurately (Hatae et al. 2012a, 2012b).

2.2.2 Discoloration

The surface texture and other surface properties of wood are important when it is used as an indoor material for housing and furniture and under external conditions. These features include color, texture and gloss. Due to the presence of extracts, heartwood usually shows a darker color than sapwood, which occurs in different wood varieties. The wood darkens under light exposure. Wood changes color when it is exposed to light (Hon 1991, Feist and Hon 1984, Pandey 2005b).

Wood is a good VU absorber. Ultraviolet light penetrates about 75 mm, and visible light penetrates about 200 mm, initiating photochemical reactions, mainly in lignin, leading to photochromism and photodegradation of the cell wall polymers (Hon 1991). Among the constituent polymers, lignin is a good light absorber with an absorption peak of 280 nm and a tail extending in the visible region up to 400 nm, so lignin is most easily degraded. The formation of free radicals originates from the absorption of light by lignin. These free radicals react with oxygen to produce chromogenic carbonyl and carboxyl groups, which are responsible for color changes (Hon 1991, Feist and Hon 1984). The fading rate depends on the wavelength, temperature and intensity of the light source. The color usually darkens under illumination. The color changes from light yellow to light yellow to brown and then turns gray (Feist and Hon 1984).

Some artificial weathering experiments have investigated the discoloration of wood by ultraviolet radiation (Hon 1991, Feist and Hon 1984, Kudo and Saito 1980,

Hon et al. 1986, Sundqvist 2002, Ohkoshi 2002, Ayadi et al. 2003, Ishiguri et al. 2003). The photodegradation of lignin showed a rapid decrease in the lignin content accompanied by the formation of carbonyl groups, while the degradation of cellulose showed a decrease in weight and the polymerization degree. In addition to the polymeric components of the cell wall (cellulose, hemicellulose, and lignin), there are many compounds that exist in wood, called extraction materials. Although these compounds account for only a low percentage of the total mass of wood, they have a significant impact on some properties of wood. These extracts from hardwood include terpenes, phenols, xylophenols, tannins, and flavonoids. These extracts are excellent light absorbers, most of which are absorbed throughout the visible range for light reactions and contribute to photochromic wood. Extract-rich wood can be bleached before a noticeable browning. Derbyshire et al. (1996) hypothesized that degradation was not strongly affected by the nature and content of the extract. Kudo and Saito (1980) reported that the photochromic rate of heartwood containing extracts was higher than that of sapwood. Some scholars have also studied the color change of heat-treated wood under ultraviolet radiation (Sundqvist 2002, Ayadi et al. 2003, Ishiguri et al. 2003).

The influence of weathering on the color and chemical composition of the wood surface was studied. The color change of the wood surface during photodegradation was analyzed by measuring CIELAB parameters (L*, a*, b* and ΔE*) (Robertson 1977). The chemical changes caused by weathering were studied by infrared and fluorescence spectra. Weathering modified the physical and chemical properties of the wood surface, resulting in rapid discoloration of the wood surface, degradation of lignin and increased concentration of discoloration groups. In general, Fourier transform infrared spectroscopy (FTIR) measurements showed that color changes (△E* values) were closely related to lignin degradation and the relative increase in carbonyl concentration. The discoloration caused by weathering is related to the formation of carbonyl groups (Pandey 2005a).

2.3 Effects of heat treatment on the weatherability of wood

Most modification methods can improve the dimensional stability and biological resistance of wood to some extent. However, few of these methods can protect wood from weathering and only a few can stabilize lignin. Modified lignin does not photodegrade easily, and modification is an obvious way to improve the photostability and weathering resistance of wood (Evans 2009).

At present, replacing harmful traditional wood protection methods with environmental protection methods has become the focus of the wood protection industry. Thermal modification is an environmentally friendly method for wood conservation because modified wood does not contain any chemicals or harmful substances. The demand of thermal modified wood is increasing day by day. Wood polymers can be modified or reconstituted by exposure to high temperatures at different times in an inert gas medium. The main advantages of thermal modification are increased hydrophobicity, improved dimensional stability, reduced equilibrium moisture content, uniform color, and better resistance to microorganisms and weathering degradation (Sandak et al. 2015, Metsä and Viitanen 2015, Turkoglu et al. 2015). Therefore, the purpose of thermal modification is to improve the service life of wood under outdoor conditions.

2.3.1 Thermal modification of wood

In thermally modified wood, the physical and chemical properties change significantly by exposing the wood to high temperatures (180–250°C) under inert or restricted air conditions. Most processes typically use temperatures in excess of 160°C, although heating wood at temperatures slightly higher than 100°C for an extended period of time can result in weight loss and performance changes. Thermal modification resulted in a decrease in the hemicellulose amorphous polysaccharide content. Condensation and demethylation of lignin also occurred (Esteves and Pereira 2009, Tjeerdsma 1998, Nuopponen et al. 2004a). Although hemicellulose is mostly affected by thermal treatment (especially at lower temperatures), other macromolecular components are also degraded (albeit to a lesser extent) at temperatures higher than 100°C.

Compared with unmodified wood, heat-treated wood has better dimensional stability and durability, but the strength performance decreases (Welzbacher et al. 2009). The water vapor adsorption performance of wood has also been significantly improved. Mechanical strength loss, brittleness and cracking are the main disadvantages of thermal modification (Metsä and Viitanen 2015, Altgen et al. 2015). Thermally modified wood has reduced mechanical strength, impact resistance and wear resistance and is not suitable for load-bearing applications. Results of wood heating are slightly improved with respect to the MOE. If heating continues, the MOE will subsequently decrease (Dirol and Guyonnet 1993, Tjeerdsma 1998, Sivonen et al. 2002, Bekhta and Niemz 2003, Nuopponen et al. 2004, Esteves et al. 2007, Brischke et al. 2007, Kocaefe et al. 2008a, Esteves et al. 2008, Esteves and Pereira 2009, Gonzalez et al. 2009).

In addition, heat-treated wood has a uniform dark color. Thermally modified wood is much darker than unmodified wood. When wood is exposed to external conditions, color changes are not permanent. However, despite the improved corrosion resistance, this is not sufficient to allow heat-modified wood to be used arbitrarily in contact with

the ground. Changes in performance are strongly influenced by the treatment methods used, such as higher temperature, longer heating time, and enhanced degradation due to heating under oxygen or steam. Heating in unventilated systems can also lead to faster degradation (Sandak et al. 2015, Metsä and Viitanen 2015, Turkoglu et al. 2015).

The effect of thermal modification on wood photostability and weathering resistance has attracted much attention. Thermal modification improves the dimensional stability and corrosion resistance of the wood, which can be used in outdoor ground applications (Giebeler 1983, Militz 2008). In these applications, thermally modified wood is exposed to weather and is usually not coated (Ala-Viikari and Mayes 2009). The short-term color stability of heat-treated wood under artificial ultraviolet irradiation is better than that of untreated wood (Ayadi et al. 2003). It has been reported that the lignin on the surface of thermally modified wood is slightly less sensitive to photodegradation than that on the surface of unmodified wood. It may be due to the increase in lignin polycondensation caused by heat treatment (Nuopponen et al. 2004). Results vary in the literature on whether thermal modification reduces wood sensitivity to cracks when exposed to outdoor conditions (Vernois 2001, Ja¨msa¨et al. 2000, Feist and Sell 1987).

2.3.2 Practicability

Thermally modified wood, commonly considered a green substitute for tropical hardwood and pressure-treated wood, can be used indoors and outdoors, such as for decks, wall panels, floors, garden furniture, and walls and ceiling panels in a sauna. Heat-treated wood can be used for outdoor applications. However, the properties of thermally modified wood under UV irradiation are still partially unknown. Understanding the behavior of thermally modified wood under ultraviolet radiation is important for its outdoor application (Srinivas and Pandey 2012).

Most of the previous research studied the weathering properties of thermally modified wood under laboratory conditions. Natural weathering tests usually take many

years and involve outdoor risks such as sample loss, fire damage, and storms. Laboratory artificial weathering tests include UV and tidal circulation. These tests are generally accepted as simulating outdoor conditions. Studies on the resistance of thermally modified wood to artificial weathering show that, compared with unmodified wood, thermally modified wood has improved color stability and surface quality and reduced cell wall degradation (Ayadi et al. 2003, Mitsui 2004, Deka et al. 2008, Srinivas and Pandey 2012, Huang et al. 2012, Yildiz et al. 2013, Xing et al. 2015, Todaro et al. 2015). However, weathering periods seem to play a key role in these findings. It has been reported that the longer the artificial weathering exposure time, the worse the color stability, surface quality, surface structure and mechanical strength of thermally modified wood (Srinivas and Pandey 2012, Huang et al. 2012, Yildiz et al. 2013, Xing et al. 2015).

However, in real life, there are many other outdoor degradation factors, including microbial colonization, aerosols, mechanical effects of wind, etc. Therefore, not only laboratory experiments but also outdoor exposure tests on and above the ground are essential for predicting the service life of wood under different service conditions (Metsä and Viitanen 2015, Brischke and Meyer 2015). Surface weathering and the durability of superheated modified wood under outdoor conditions have been studied in the past (Metsä and Viitanen 2015, Metsa et al. 2011, Turkoglu et al. 2015, Nuopponen et al. 2004, Tomak et al. 2014, 2018). These studies clearly show that thermally modified wood is more resistant to natural weathering factors than unmodified wood, with a smaller range of changes in surface properties.

2.4 Effect of impregnation modification on the weatherability of wood

Wood modified by resin has biodegradability resistance and shows new advantages compared with other modification techniques. Resin impregnation is an alternative to traditional preservation methods for toxic chemicals (Ryu et al. 1991, 1993, Takahashi and Imamura 1990). Low-molecular-weight resins with active alcohols and lower alkalinity have great potential as bioactive polymers to produce

durable wood materials under a low resin load (Ryu et al. 1993).

2.4.1 Resin impregnation

The principle of impregnation modification is to impregnate the cell walls of wood with a combination of one or more chemicals, which then react to form a material locked in the cell wall. The cell wall is in an expanded state during the impregnation stage to ensure the integrity of the impregnation. It is self-evident that the molecular composition of the impregnated resin should be small enough to allow resins to enter the interior of the wood cell wall. The monomer (or oligomer) is impregnated and subsequently polymerized in the cell wall. The soluble substances diffuse into the cell wall and are subsequently treated to make them insoluble.

Stamm and Seborg (1947) listed three basic criteria for effective resin treatment of wood: the size of the resin molecule must be sufficiently small; the resin can penetrate the cell wall; and the resin is required to be non-polymerized or only slightly polymerized. Resin molecules should be soluble in polar solvents so that the cell wall is swollen, thus allowing diffusion inside the cell wall. Resin molecules should exhibit sufficient polarity and thus exhibit high affinity to the cellular wall macromolecular components.

In the cell wall, fixed impregnated substances should be nontoxic. In any case (such as incineration or composting, or any recycling), impregnated substances release from the cell wall should also be nontoxic. An important factor to ensure complete penetration of the cell wall is to have sufficient time for the diffusion of impregnated molecules into the intercellular components. This is artificially allowed to last for several days (and in some cases weeks). It must be emphasized that pressure treatment will contribute to the penetration of larger wood samples, but it will not cause cell wall penetration in any way. This is a purely diffusion-controlled process. Impregnation treatments utilize vacuum and pressure processes to achieve better penetration (Archer and Lebow 2006). The absorptivity of the impregnated solution depends on the type of

wood. Because of the axial position of the cell cavity, the absorptivity is usually better in the longitudinal direction than in the radial or tangential direction (Larnøy et al. 2005).

The presence of non-leaching materials in wood cell walls can affect the physical and biological properties of wood through a variety of mechanisms. These materials cause the cell walls to swell, which gives the treated wood dimensional stability. The size of the wood can be stabilized by blocking the cell cavity, which reduces the absorption of water (Deka and Saikia 2000). The material takes up space in the cell wall, otherwise it will be used by water molecules, which leads to a decrease in wood moisture absorption. Blockage of cell wall micropores reduces the diffusion of water and other molecules into the cell wall. The deposition of insoluble substances in the cell wall structure is an effective and practical method to keep the wood cell wall structure in a partial or complete expansion state. This can be achieved by various appropriate impregnation agents such as resins and waxes. The size change due to atmospheric humidity can be greatly reduced by impregnation (Stamm and Tarkow 1947).

The hydroxyl content of some cell walls is masked. This may be a contributing factor to the reduction of water vapor adsorption. A cell wall expander can react with the polymer component of the cell wall to produce cross-linking. If the molecule is too large to penetrate the cell wall, it will form a barrier on the cavity surface to prevent the entry of the decomposing agent. Similarly, this obstacle may break down over time. In impregnation modification, the wood substrate is filled with inert materials, resulting in expected performance changes (Hill 2006).

2.4.2 Current application

Thermosetting resins have been used to develop some wood polymer composites with commercial applications. Compression and impregnation treatments were developed in the United States in the 1960s. These treatments were impregnated in phenolic resin into the wood structure. After curing, wood resistance to decay, termites and marine borers was improved. Impregnation treatment involved phenolic resin

impregnation of wood. Curing at high temperatures, this method kept the cell wall permanently swollen (Stamm and Seborg 1962). However, compression treatment is where the wood is impregnated in the phenolic resin and solidified at high temperature to reduce shrinkage and expansion and to increase density and strength (Stamm and Seborg 1951). The processed product has been used to make knives and tool handles, music or electronic instruments.

Vinyl monomer leaching and in situ polymerization are other promising methods to improve mechanical properties, dimensional stability and thermal stability, as well as antifungal and insect-resistant properties of low natural durability. Various commercially available vinyl monomers have been studied, including acrylonitrile, glycidyl methacrylate, methyl methacrylate, hydroxyethyl methacrylate, ethylene glycol dimethyl acrylate, butyl acrylate, butyl methacrylate, styrene, acrylamide, and acrylonitrile (Mathias and Wright 1989, Şolpan and Güven 1998, 1999a, b, c, d, Devi et al. 2004, Zhang et al. 2006, Ajji 2006, Devi and Maji 2007, Kumar et al. 2008, Li et al. 2010). Depending on the nature of the monomer used, polymerization can occur either in the cell cavity or in the cell wall or simultaneously (Mathias and Wright 1989, Schneider 1995, Cleland et al. 2009). Polymerization can be performed in different ways using a thermal radical initiator or gamma radiation. Different researchers reported that gamma radiation was an effective way to initiate polymerization (Thomas et al. 1993; Sheikh and Taromi 1993, El-Awady 1999, Ajji 2006, Gago et al. 2007). X-rays generated by high-energy and high-current electron beams can also be used to initiate in situ polymerization of vinyl monomers. The X-rays initiated polymerization and penetrated thick wood flakes. During the polymerization of wood chips, the monomers in the cell wall of wood chips were polymerized. These radiation curing treatments entered the cell wall and then polymerized inside the cell wall, increasing the dimensional stability of the treated wood (Cleland et al. 2009).

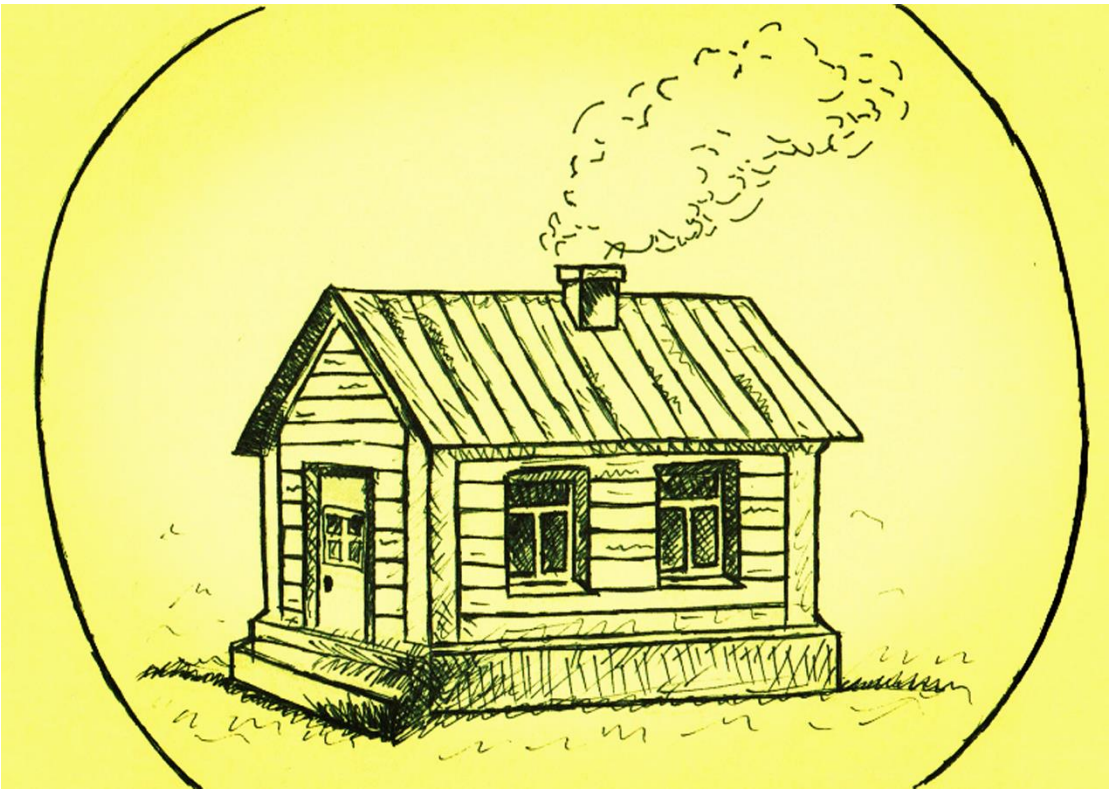
The following researchers reported the effect of using melamine formaldehyde resin. Gindl et al. (2003) studied the penetration of melamine formaldehyde resin in

softwood. It was found that a high cell wall moisture content, high resin moisture content and low extract content were the favorable factors for the successful absorption of melamine into the cell wall. Lukowsky (2002) suggested that melamine resins with a low or high formaldehyde content had better permeability in the cell wall due to their low condensation degree. Hansmann et al. (2006) claimed that melamine could protect solid wood from weathering while maintaining the natural appearance of wood. Melamine treatment reduced the water absorption of solid wood, which had a positive effect on the dimensional stability and improved the strength and corrosion resistance of wood (Hansmann et al. 2006).

2.5 Conclusion of the literature review

The review has revealed that through the understanding of wood durability, in order to prevent wood deterioration, a more effective protection system for wood should be established and improved. The weathering behavior of different tree species is different, which is closely related to their wood characteristics. Natural weathering is a long-term observation experimental process. However, the weathering behavior of a tree species can be obtained in a short time by observing the changes in the wood surface structure and characteristics. The protection and treatment of wood by environmental protection methods have become the focus of attention in the wood industry. Thermal modification is one of protection methods. At present, thermally modified wood has better physical properties than untreated wood, but the loss of mechanical strength cannot be ignored. Previous studies have shown that heat-treated wood is feasible in the field of weathering resistance, but it still needs to be further explored. Wood modified by non-toxic resin has the characteristics of weathering resistance and degradation, which also shows new advantages and has attracted wide attention.

CHAPTER 3 Weathering Behavior of *Cunninghamia lanceolata* (Lamb.) Hook. under Natural Conditions



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3.1 Abstract

Information on the weathering behavior of *C. lanceolata* is needed to provide references for wood weatherproof pre-treatment and to improve wood utilization. Therefore, this study was conducted to understand the variation in the intrinsic weathering behavior of *C. lanceolata* under natural conditions. Wood samples from 15 *C. lanceolata* trees aged 26–30 years old were used. The structural degradation and discoloration of wood surfaces before and after exposure were compared. The results show that the weathering behavior of wood was weakened from heartwood to sapwood and enhanced from the bottom to the top. This study provided information for weatherability research and improved wood utilization of *C. lanceolata*.

Keywords: *Cunninghamia lanceolata*; weathering; density; color change; wood structure

3.2 Introduction

C. lanceolata is a member of the family Cupressaceae. It is an evergreen tree that can grow up to 50 m in height and over 3 m in diameter. It forms mixed broad-leaved forests or small, pure stands, rocky hillsides, roadsides, with altitudes ranging from 200 to 2800 m (Fu et al. 1999). It grows naturally in China, Laos, Vietnam, Malaysia, and Cambodia. Plantations have been established in countries including Argentina, Japan, New Zealand, South Africa. It adapts to the climatic conditions with an annual average temperature of 16–19 ◦C, extreme minimum temperature of -15 ◦C, and annual precipitation of 900–2350 mm. Its advantages are excellent material properties, attractive scent, moderate hardness, straight texture, and easy processing. In China, *C. lanceolata* accounts for 20%–30% of the total commercial timber production (Ken 2020, Jøker 2000, Orwa et al. 2009). In recent years, about 400,000 ha. of plantations have been established annually by seedlings and cuttings in Southeastern China (Minghe et al. 1999).

C. lanceolata has a fragrant smell and contains cedar camphor (Zhou et al. 2007). After the decay test using *Postia placenta* and *Trametes versicolor*, *C. lanceolata* was classified as a slightly durable wood. It showed moderate resistance to termites either in the laboratory or in the field (Xing et al. 2005). It has been widely used for constructing buildings, bridges, ships, and lamp posts in furniture manufacturing and for producing wood fibre (Fu et al. 1999, Jøker 2000, Orwa et al. 2009). Therefore, *C. lanceolata* is extensively used in outdoor environments. For example, it has been used as the main building material of Chinese Dong minority drum towers and wind and rain bridges (Luo et al. 2019, Cai et al. 2016). Despite the multiple studies on the wood properties of *C. lanceolata*, there are still many unknowns regarding its weathering. Studying the weathering behavior is important because it can aid in determining the most effective treatment methods and guide the establishment and refinement of *C. lanceolata* weathering protection methods.

Differences in weathering behavior exist among various species (Hon et al. 1986, Evans 1988, Anderson et al. 1991, Nzokou et al. 2011, Agnieszka 2013, Zborowska et al. 2014, Jankowska et al. 2014). According to the variation in the wood properties of different positions within the same tree species (Akachuku et al. 1984, Qatanabe et al. 1998, Ivkovi´c et al. 2009, Hasegawa et al. 2011, Borrega et al. 2015), it is inferred that there are also differences in degradation characteristics inside the wood. The study of natural weathering usually involves a long-term research study. Problems such as missing samples during experiments would affect the accuracy of experimental results. However, differences in artificial weathering test results occurred in previous research studies, and these tests cannot completely replace natural weathering (Williams 2005, Buchner 2018). In the current study, the effects of weathering on wood began with the exposure of samples to natural conditions (Evans et al. 1996, Tolvaj et al. 2009). Effects of weathering on wood could be obtained in a short period by focusing on the changes in the wood surface. The purpose of this study is to clarify the variation in intrinsic weathering behavior of *C. lanceolata*. We completed a short outdoor exposure experiment and observed the aging differences within trees of *C. lanceolata* along the radial and axial directions. To attain these objectives, color and anatomical structure were used to compare and analyse changes in the surface of the wood. This study obtained information on degradation characteristics, which provided references for the study on the weatherability of *C. lanceolata.*

3.3 Materials and methods

3.3.1 Wood sample preparation

Fifteen trees aged 26–30 years and without any major defects were selected. Each tree sample was cut from a 2.5 cm thick log at 1, 2, 3, and 4 m above the ground. The surfaces of the samples were smoothed by sanding with abrasive paper. As shown in Figure 3.1, for the selected samples, the grain was required to be straight, and there were no nodes or visible defects.

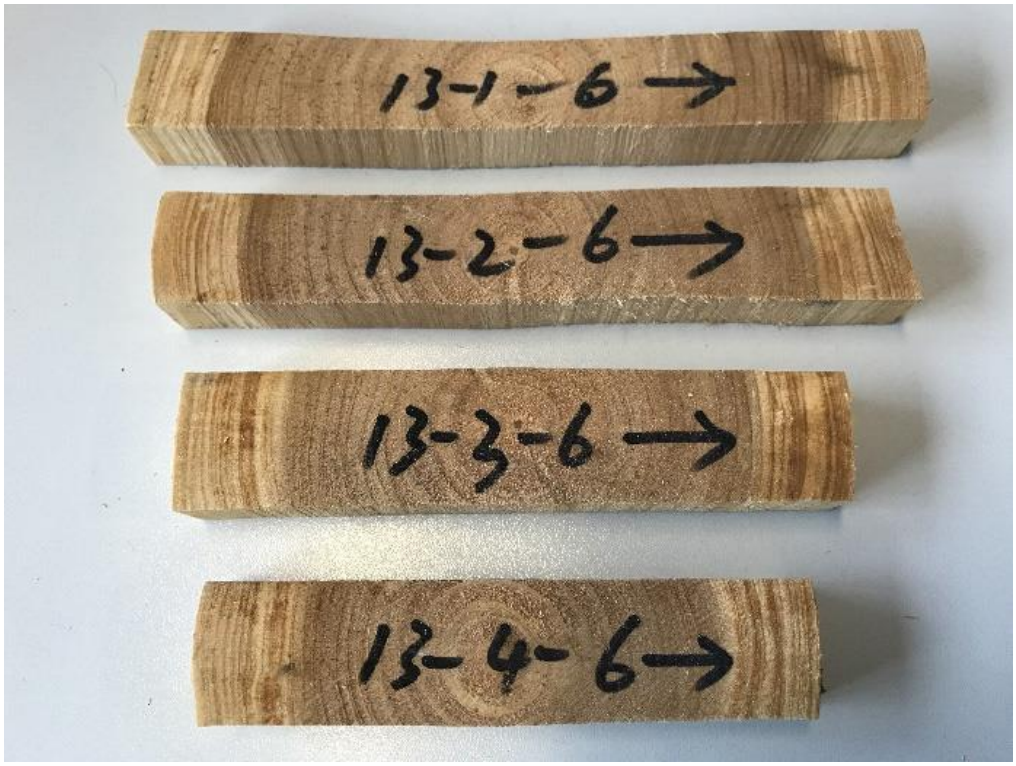


Figure 3.1 Samples were cut through the pith from *C. lanceolata* (at 1, 2, 3, 4 m heights).

3.3.2 Wood Density

As shown in Figure 3.2, due to the different growth rings, at 1, 2, 3, and 4 m from the ground, a sample of each of three growth ring position was cut to measure the density of the wood. The total sample number of this experiment was 540.

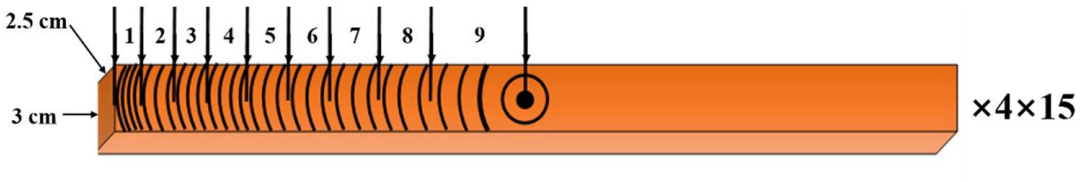


Figure 3.2 Samples for wood-specific gravity testing.

Wood density measurement samples were placed in a conditioning room at 20 °C and 65% relative humidity. The moisture content of wood was maintained at 10%–12%. The instrument used to measure density was an electronic densimeter (MD-300S, Alfa Mirage, Tokyo, Japan). The device adopted Archimedes' principle and the determination of the value of relative density was based on a 1 g/cm3 water density at 4 °C. As shown in Figure 3.3, the measurement procedure was as follows. Firstly, the sample was weighed. Secondly, it was placed in water. Finally, the density of sample was calculated to be stable. In this experiment, each sample took roughly the same amount of time to enter the water, and the values quickly reached equilibrium. Therefore, the effect of the wood absorbing water was ignored. In total, 540 samples were measured by this method.

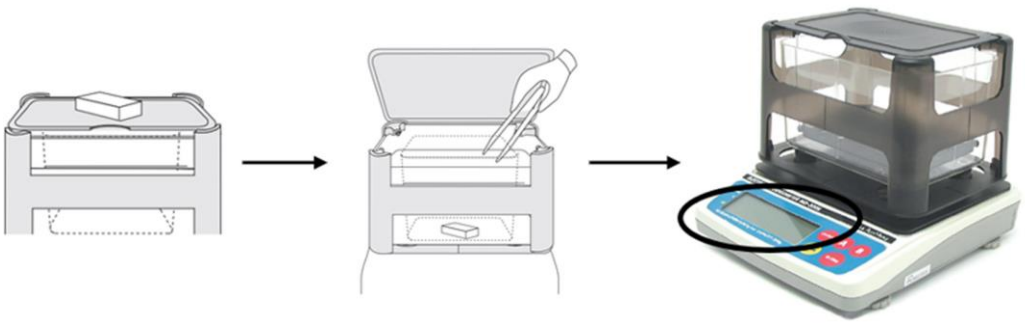


Figure 3.3 The procedure of the measurement of density.

3.3.3 Weathering Conditions

Samples were exposed to natural conditions over a period of 30 days. The samples were placed outdoors in a complete block design, facing equatorially (south), and at an angle of 45◦ to the horizontal, in Fukuoka (latitude 33◦ north), Japan, during the summer of 2017, as shown in Table 3.1. Fukuoka has a humid subtropical climate. The Scheffer index values of Fukuoka are in the range between 82 and 95 using 50 years climate data (1969 to 2019) (Scheffer 1971). At the end of 6 days of exposure, all of the specimens were retrieved from the weathering racks and measured in a laboratory, after which they were placed back on the racks. This process was repeated after 12, 18, and 30 days of exposure (Kataoka et al. 2009). After each exposure, all of the samples were lightly blown with nitrogen to remove dust from the exposed surfaces.

Table 3.1 Weathering conditions in Fukuoka during summer 2017.

Weather Condition	Temperature (°C)	Humidity (%)	Sunshine Duration (h)	Rainfall (mm)	Wind Speed (m/s)
Mean value ± SD	29.42 ± 1.40	74.98 ± 6.97	7.51 ± 3.37	3.90	2.93 ± 0.77

Note: the parameters show the average and standard deviation (SD) during July and August 2017 (N =62).

3.3.4 Low-Vacuum Scanning Electron Microscopy

As shown in Figure 3.4, the heartwood and sapwood samples were cut into 10(R) × 10(T) × 10(L) mm small wood samples at axial heights of 1–4 m. This size sample was obtained for 120 blocks. Microstructure observation samples were cut using a sledge microtome to reveal three sections at different samples, and the cut samples were placed in a 60 ◦C dry environment.

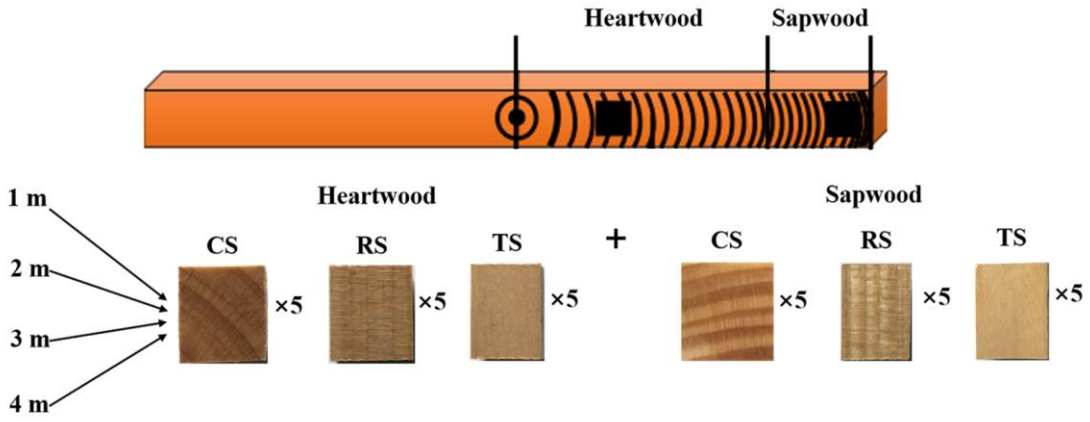


Figure 3.4 Microstructure observation samples were cut into 10(R) × 10(T) × 10(L) mm

Uncoated samples were observed by low-vacuum scanning electron microscopy (LVSEM, JEOL JSM-5600LV, JEOL, Tokyo, Japan) before and after natural exposure. The conditions were as follows: voltage 15 kV; pressure 10–30 Pa; and working distance, under 10–20 mm (Hatae et al. 2012a, 2012b). The same surface was repeatedly analysed before exposure and at the end of each alteration period.

3.3.5 Color Measurements

Color measurements were used to evaluate the color change of wood surfaces before and after each period of natural exposure. The samples' size was the same as the microstructure observation samples. The color measurements were performed on tangential sections of each sample. The preparation of 80 samples is shown in Figure 3.5; 30 measurements were performed per sample.

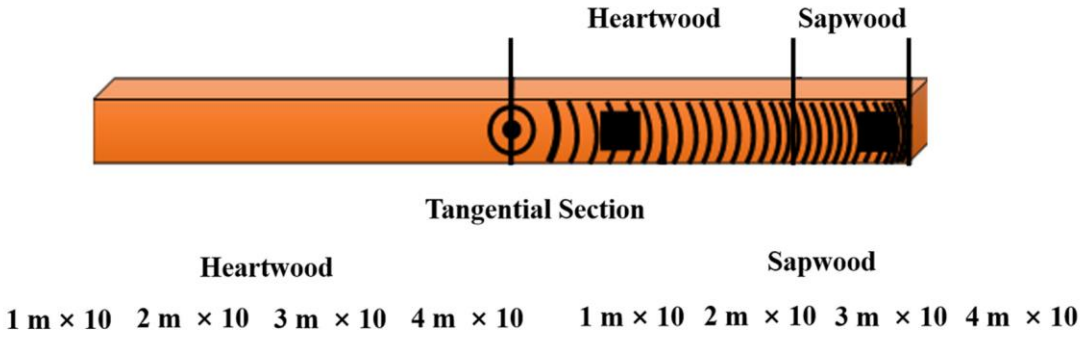


Figure 3.5 Color measurement samples.

A Nippon Denshoku handy colorimeter (model NR-3000, Nippon Denshoku, Tokyo, Japan) was used to measure color with the CIE L*a*b* system (Cao et al. 2012). This system evaluates color based on three parameters: lightness coordinates, with L* and +L* for lighting and -L* towards darkening; and the chromaticity coordinates a* and b*, with +a* for red, -a* towards green, +b* for yellow, and -b* towards blue. The L*, a*, and b* color coordinates for each sample were determined before and after exposure to natural conditions. The degree of color change was measured on a color measurement device by the standard illuminant D65 and standard observer 2◦. The average values and standard deviation values were computed for each sample. These values were used to calculate color change with the following formulas.

$$C* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

$$\triangle C^* = C^* - C_o^* \quad (2)$$

$$\triangle E^* = \sqrt{\triangle L^{*2} + \triangle a^{*2} + \triangle b^{*2}} \quad (3)$$

$$\triangle H^* = \sqrt{\triangle E^{*2} - \triangle L^{*2} - \triangle C^{*2}} \quad (4)$$

where ΔL*, Δa*, and Δb* are the respective changes in L*, a*, and b* between the unexposed and exposed interval values. C* indicates chroma, while ΔC* indicates the chroma difference. ΔE* describes the total color-difference value and ΔH* denotes hue difference (Robertson 1977, Tolvaj et al. 1995).

3.4 Results and Discussion

3.4.1 Wood Density

Table 3.2 summarizes the data of wood density along the axial direction. The density of wood in the axial direction decreased from bottom to top, which agrees with the auxin gradient theory of wood (Missanjo et al. 2016, Larson 1969). These results agree with previous studies (Yin et al. 2011). Ren et al. indicated that the density of *C. lanceolata* was 0.366–0.356 g/cm3 from bottom to top (Ren et al. 2006).

Table 3.2 Variation of wood density along the stem height direction with standard errors.

Variable	Description	*n*	χ ± s	F	*p*
Stem height (m) above ground	1	135	0.371 ± 0.042	1.497	0.216
	2	135	0.362 ± 0.044		
	3	135	0.358 ± 0.039		
	4	135	0.357 ± 0.044		

3.4.2 LVSEM Analysis

Weathering usually refers to the slow degradation of materials when exposed to the natural environment. It can be influenced by sunlight, moisture, temperature, wind, air pollutants and other factors (Williams 2005). In fact, the wood surface changes of weathering behavior begin from the moment the wood is exposed outdoors. According to the report, the surface characteristics of wood experience significant changes in a short exposure time (Evans et al. 1996). Weathering of the wood surface could cause changes in color, chemistry, physics, and anatomical structure. These changes are evident up to 0.5 mm below the surface during the initial period of weathering (Roger et al. 2000). Therefore, the analysis of wood surface changes in a short period of time can also be used as a method to evaluate the weatherability of wood.

Deterioration of wood surfaces at the microscopic level during the natural weathering of the samples was observed by scanning electron microscopy (SEM). This method is a valuable tool for observing the microscopic anatomical details of degraded wood, including the cell wall shape, and evaluating changes in the cell wall. It provided deterioration information about the surfaces. The surface deterioration of the exposed wood can be observed by LVSEM. The advantage of this method is that the information is obtained intuitively and accurately (Hatae et al. 2012a, 2012b). The photodegradative effects on cross-sections and radial sections when the samples were exposed to natural weather for 30 d are described below (Figures 3.6–3.8).

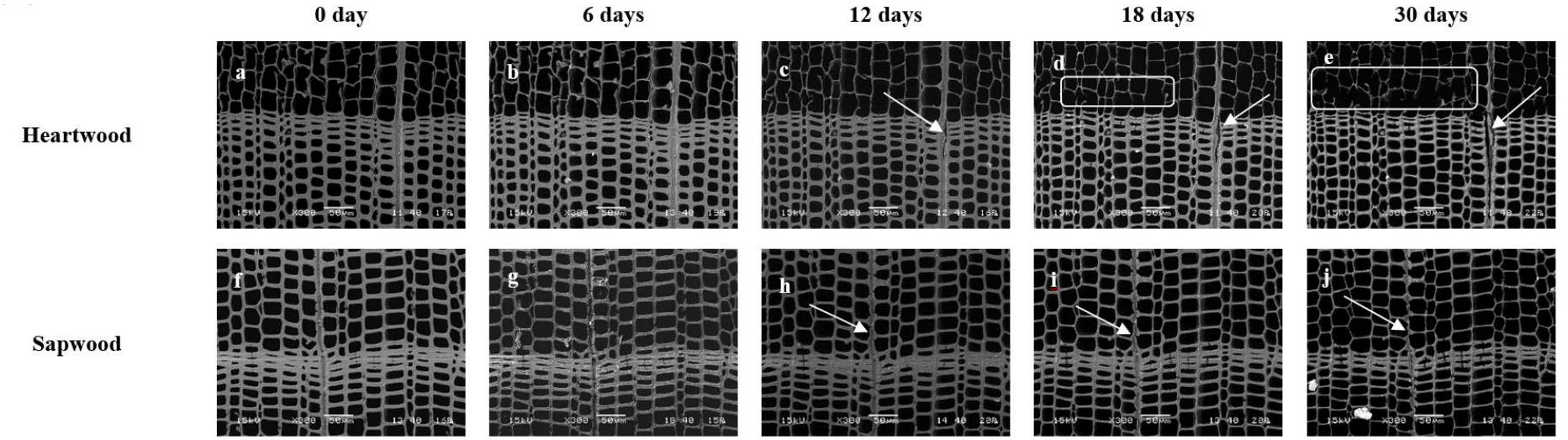


Figure 3.6 Low-vacuum scanning-electron-microscopy (LVSEM) micrographs (×300) of cross-sections (1 m height) of heartwood and sapwood before and after weathering. (Unexposed heartwood and sapwood surfaces were (**a**) and (**f**); (**b**–**e**), were cross-sections of heartwood after exposure 6,12,18, and 30 days; (**g**–**j**), were the surfaces of sapwood after 6,12,18, and 30 days.) The arrows and squares in the figures showed that the areas of significant change in microstructure were affected by weathering.

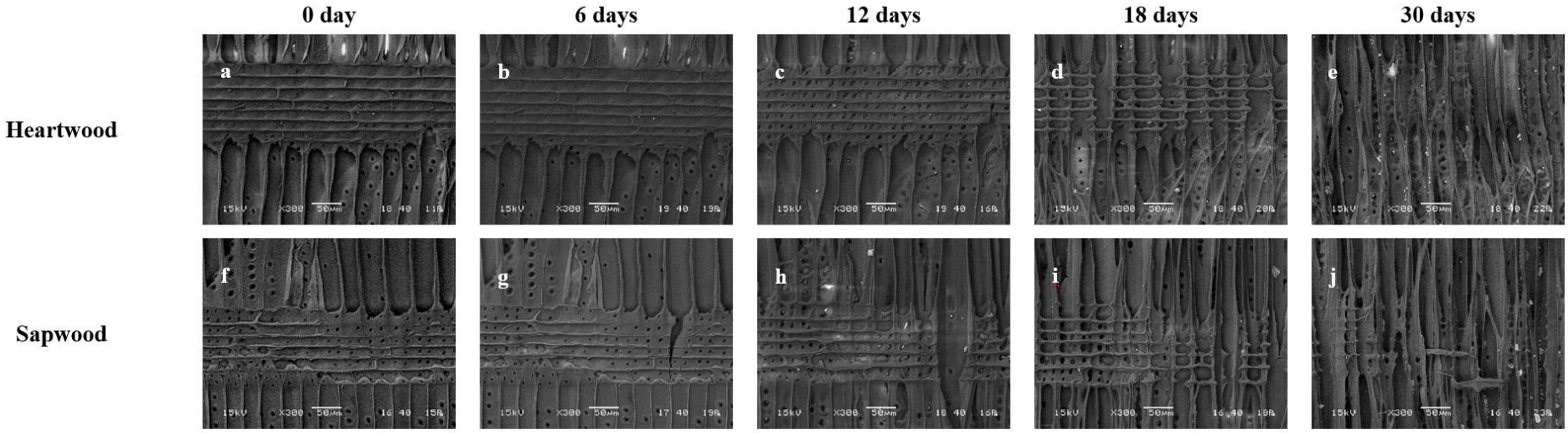


Figure 3.7 Low-vacuum scanning-electron-microscopy (LVSEM) micrographs (×300) of radial-sections (1 m height) of heartwood and sapwood before and after weathering. (Unexposed heartwood and sapwood surfaces were (**a**) and (**f**); (**b**–**e**) were radial-sections of heartwood after exposure 6,12,18, and 30 days; (**g**–**j**) were the surfaces of sapwood after 6,12,18, and 30 days.)

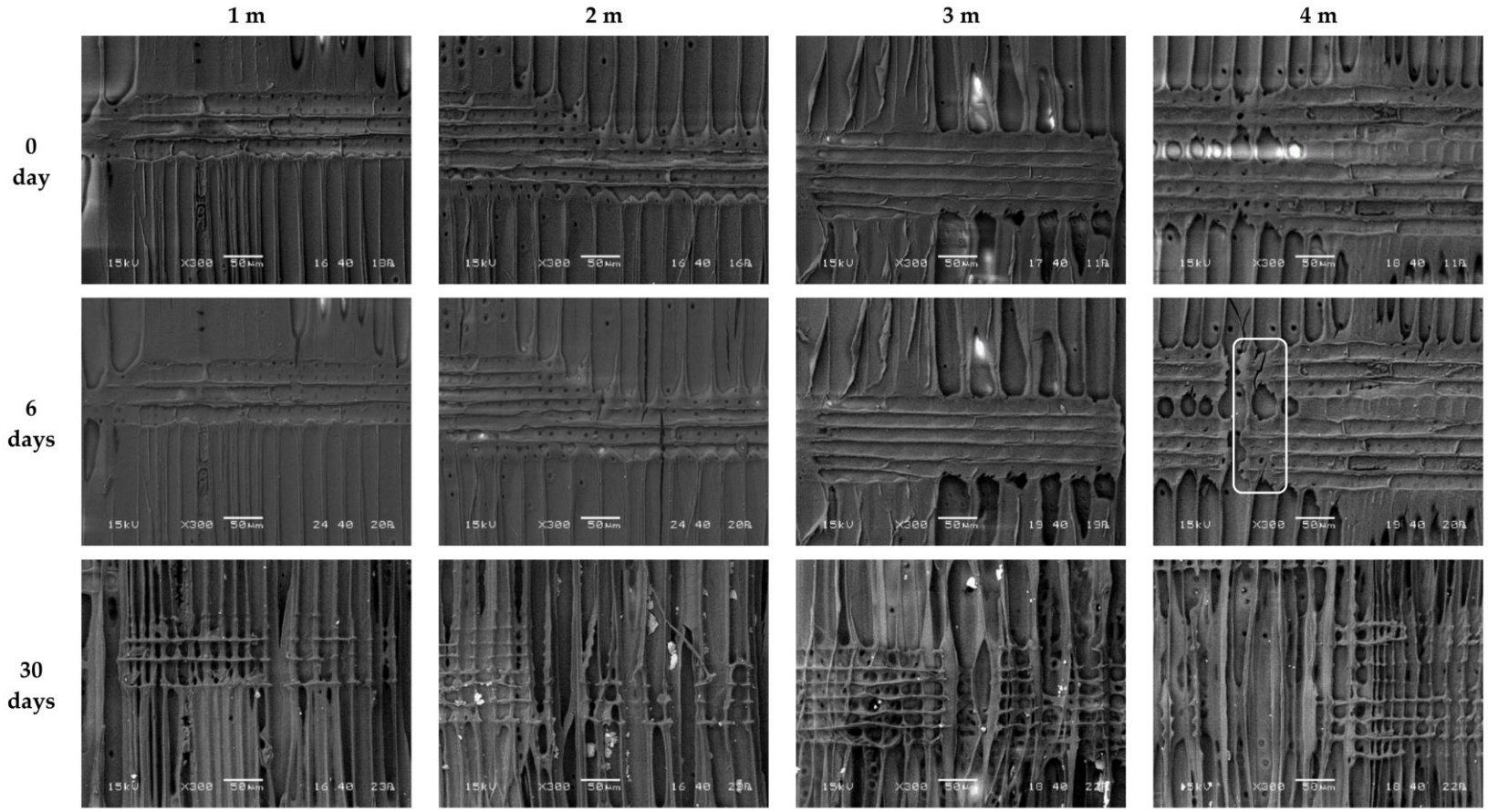


Figure 3.8 Low-vacuum scanning-electron-microscopy (LVSEM) micrographs (×300) of radial-sections of different-height *C. lanceolata* before and after weathering. The square in the figure showed that the area of significant change in microstructure was affected by weathering.

Figure 3.6 shows LVSEM micrographs comparing the cross-sections of *C. lanceolata* heartwood and sapwood before weathering (Figure 3.6a, f) with those after 6 days (Figure 3.6b, g), 12 d (Figure 3.6c, h), 18 d (Figure 3.6d, i), and 30 d (Figure 3.6e, j) of exposure. The surface of the wood exposed for 30 d was rougher, and four significant changes were discernible: significant loss of the middle lamella, separation of cell walls, wastage of the ray cell walls, and cell wall degradation of earlywood and latewood (as shown by the arrows in the figures). Each of these phenomena proved that further exposure resulted in more distinct changes and characteristics of the degradation process. In a previous study (Miniutti 1967), comparable photodegradation was observed in wood that had been earlier exposed to long-wavelength UV radiation (300–400 nm).

The LVSEM micrographs of radial *C. lanceolata* surfaces are shown in Figure 3.7. Intact bordered pits could be observed on radial sections in both earlywood and latewood before natural weathering. The pit structures in the radial section appeared to crack after 12 days of natural weathering. The bordered pit is mainly composed of pectin and cellulose, which contain some phenolic substances (Bauch et al. 1973, Maschek et al. 2013). With prolonged exposure, the phenolic substances were oxidized, and the pits cracked. Moreover, the deterioration also spread over the radial section of the tracheid walls, and roughening of cell walls was also noticed. In addition, the decrease in structural integrity was more significant in the cross-field. As seen in Figure 3.7d, the cross-field was entirely destroyed. After 30 d of exposure, the wood radial section structure was completely destroyed, especially on the heartwood surface. Compared with the cross-section, the decay of the radial section was faster and more pronounced.

Photodegradation has been found to be closely related with the change in the wood surface's chemical composition (Williams 2005, Pandey 2005). Based on known research, the chemical composition of softwood is distributed as follows (Rowell et al. 2005): The middle lamella and the primary wall are mainly composed of lignin (84%),

hemicellulose (13.3%), and cellulose (0.7%). The S1 secondary wall layer contains 51.7% lignin, 30% cellulose, and 18.3% hemicellulose. The S2 layer is composed of 54.3% cellulose, 30.6% hemicellulose, and 15.1% lignin. The S3 layer has 87% hemicellulose, 13% cellulose, and little or no lignin. From Figures 3.6 and 3.7, the structures of the middle lamella and primary cell wall were initially broken down during natural weathering, such as the primary cell wall of parenchyma. This is consistent with the conclusions of many academics, and lignin has always been reported as the most sensitive chemical component in wood photodegradation (Evans et al. 1996, Pandey 2005, William et al. 1984). Through the observation of the cell wall degradation on the cross-section, it was found that only the skeleton structure remained after one month of natural weathering. Cellulose, hemicelluloses, and lignin are skeletal substances in wood. Cellulose, a basic skeleton material, is responsible for wood strength. Hemicellulose and lignin together are matrix systems in wood, and lignin provides wood with rigidity or stiffness. Absorption of UV light by lignin on or near the wood surface causes the preferential degradation of lignin, followed by the degradation of hemicellulose and cellulose. Cellulose is more photodegradation-resistant than hemicellulose due to its high molecular weight and protection by its crystalline structure (Kollmann et al. 1975, Shmulsky et al. 2019). The graphical result was consistent with the conclusion that the cellulose was the last to photodegrade.

The changes in the anatomical structure of heartwood and sapwood before and after weathering were compared as well. The results show various effects of weathering on heartwood and sapwood. The anti-weathering ability of the surface structure of heartwood was found to be lower than that of sapwood. Li et al. found that the heartwood cellulose content (48.6%) of *C. lanceolata* is lower than that of sapwood (52.0%) on average (Li et al. 2019). Therefore, the photodegradation of heartwood after 30 days was more serious, as shown in Figures 3.6 and 3.7.

The LVSEM micrographs in Figure 3.8 show that during the weathering process the surface structure of *C. lanceolata* changed in different heights. After weathering for

one week, the surface structure of *C. lanceolata* began to degrade; the change at the 4 m height was especially obvious (Figure 3.8h). One month later, the wood surface was severely damaged. The comparison of micrographs (Figure 3.8i–l) indicated that the damage at the 1 m height was the slightest, while that at the 4 m height was slightly severe. The variation in the wood surface structure along the axial height was slightly different. It is inferred that the bottom material of *C. lanceolata* has better weatherproof performance than the top material.

The correlation between density and weathering behavior of *C. lanceolata* was found in Table 3.2 and Figure 3.8. It was found that the weathering behavior of *C. lanceolata* was also positively correlated with the wood density; where the density was relatively high, the weatherproofing was strong, and vice versa. It can be concluded that weathering resistance is related to the characteristics of *C. lanceolata*. Improving the basic properties of wood (e.g., density) would have a positive impact on the weatherproof properties. For example, thermo-mechanical densification of wood can improve the dimensional stability and durability of wood (Welzbacher et al. 2008).

3.4.3 Discoloration of Wood Surface

The color of the wood is influenced by light radiation, rainwater, and temperature, among other factors. In particular, UV light causes remarkable color changes. Wood absorbs light and interacts with polymeric compounds and photons. This property leads to deterioration and discoloration when the wood is exposed to natural conditions. The change in wood color reflects the change in the wood chemical composition during photodegradation. Color stability is an important wood parameter (Tolvaj et al. 1995, Mitsui et al. 2005, Mikleˇci´c et al. 2011, Rüther et al. 2013).

When the samples were exposed to a natural environment for one month, a significant color change occurred. Figure 3.9 shows the color parameters (L*, a*, b*, c*) of heartwood and sapwood surfaces at different heights when the wood was exposed to natural conditions. The lightness value (L*) of sapwood was much higher than that of heartwood before exposure. After 6 days of initial exposure, the sapwood lightness decreased significantly, and the value was similar to that of heartwood. The value then tended to be stable, indicating that the trend of continued darkening was weakening. The lightness of heartwood showed a downward trend within 12 days of exposure, and then followed an upward trend (Figure 3.9a). This shows that the heartwood surface became darker at first and then brightened during exposure for one month. It can be seen from Figure 3.9b–d that a* (redness), b* (yellowness), and c* (chroma) increased significantly during the 6 days exposure. The maximum values were reached after the 6 days of exposure and then began to decrease. One month later, the a* (redness) was lower than that of the unexposed wood; the b* (yellowness) and chroma of sapwood were higher than those of heartwood.

In the weathering process, cellulose has little effect and does not bring obvious discoloration (Pandey 2005, Calienno et al. 2014, Wang et al. 2009). The yellowing of wood surfaces is due to the modification of hemicellulose and lignin. Lignin is more susceptible to photochemical reactions, resulting in chromogenic groups. Lignin is a

good absorbent, and its absorption wavelength can reach 400 nm with a peak value of 280 nm. Phenolic hydroxyl groups react with light quickly to form phenolic groups, which are converted to *o*- and *p*-quinonoid structures by demethylation or by cleavage of side chains and formation of carbonyl based chromophoric groups (Ren et al 2006, Rowell et al. 2005, Hon 1991). The generation of chromophoric units brings a huge change in color. In general, heartwood contains more extractives than sapwood. Therefore, the color of heartwood was darker than that of sapwood (Figure 3.9a), with higher a* (redness) (Figure 3.9b) and lower c* (chroma) (Figure 3.9d) at the initial stage.

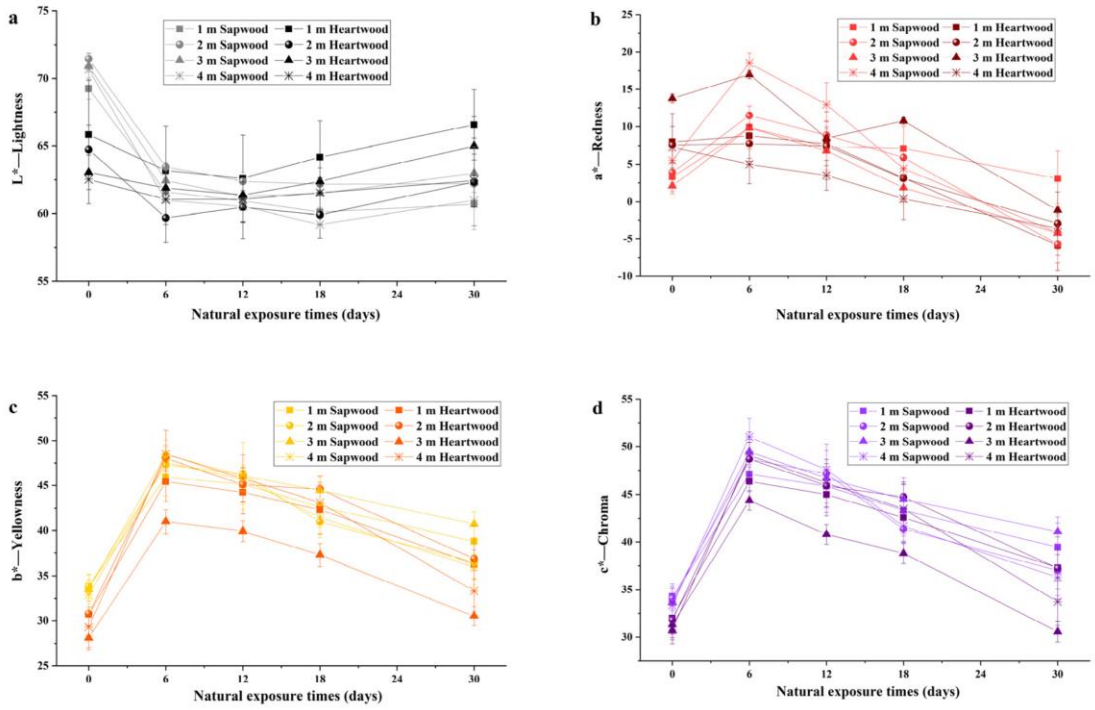


Figure 3.9 Color coordinates of *C. lanceolata* due to natural weathering: (**a**) Lightness L*; (**b**) redness a*; (**c**) yellowness b*; (**d**) chroma c*.

Table 3.3 summarizes the results of chroma difference ΔC*, total difference ΔE*, and hue difference ΔH* along the radial direction and the axial height. The results show that the color of ΔC* decreased with exposure time. By comparison, it was found that the color change values in the rectangle on Table 3.3 showed regularity within 12 days. In the axial direction, the sapwood increased with axial height, and the changes in ΔC*, ΔE*, and ΔH* were larger. According to other studies, the density towards the top

decreases due to the maturity of the bottom wood tissue. This also explains why the wood quality at the bottom of the logs was superior to that at the top. This phenomenon is consistent with the auxin gradient theory (Larson 1969). According to this theory, endogenous auxin produced by growing apical regions promotes the formation of division and xylem differentiation. Therefore, the early wood yield near the canopy is higher, resulting in a lower density of the top wood, a decrease in strength, and an increase in the relative content of lignin. The surface color of sapwood darkened over the course of the 12 days. In the radial direction, within 12 days, the chroma difference ΔC* of heartwood changed more than that of sapwood. The chroma value was lower before the exposure of the heartwood in its position. The ΔE* value of sapwood was higher than that of heartwood, and the color change of sapwood was significant in this period because the heartwood contained more extractives, which played a certain role in the resistance to photodegradation in the early stage of weathering. The current research results are consistent with a previous study (Chang et al. 2010).

Lots of references showed that color changes were the result of the changes in wood chemistry (Robertson 1977, Pandey 2005, Calienno et al. 2014, Kržišnik et al. 2018). The results of this article show that, within one month of exposure, the color change was obvious. This indicates that the decomposition of the chemical components of the wood surface intensified. Color data can be obtained quickly and conveniently. The influence of weathering on the surface of wood can be rapidly discovered after analyzed the data. This means that color change can be used as a parameter with which to predict the effects of weathering in a short period. After one month of exposure, the initial anatomical structure of the wood surface was basically completely damaged. The color and structural changes of wood surfaces during the first month of weathering are the most intuitive and accurate. The method used in this study can quickly identify the weathering characteristics of wood and can play an active role in the investigation of the effects of wood weatherproofing treatment.

Table 3.3 Chroma difference (ΔC*), total color-difference value (ΔE*), and hue difference (ΔH*) are the coordinate-average values and standard deviations (in parentheses) of *C. lanceolata* after natural weathering.

Exposure Time (d)	Height (m)	ΔC*		ΔE*		ΔH*	
		Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood
6	1	13.06 (1.83)	14.37 (2.91)	15.96 (1.71)	15.47 (2.44)	4.57 (1.60)	4.68 (0.26)
	2	14.63 (0.27)	16.89 (0.56)	17.43 (0.21)	17.92 (0.47)	4.99 (0.61)	3.11 (0.95)
	3	15.87 (0.34)	13.05 (0.12)	18.87 (0.55)	13.32 (0.09)	5.62 (1.00)	2.34 (0.41)
	4	17.68 (0.50)	18.31 (1.53)	21.86 (0.34)	19.39 (1.74)	8.43 (0.34)	5.51 (2.97)
12	1	11.80 (1.98)	13.00 (3.12)	14.84 (1.77)	14.21 (2.57)	2.62 (1.82)	3.97 (1.38)
	2	13.09 (1.20)	14.09 (1.17)	16.36 (1.29)	15.27 (1.29)	2.99 (2.15)	2.93 (2.38)
	3	13.09 (2.63)	9.49 (0.30)	16.80 (2.17)	13.07 (0.57)	3.32 (2.12)	8.77 (0.64)
	4	14.22 (0.56)	15.42 (1.15)	18.11 (1.32)	17.15 (1.12)	4.39 (2.07)	6.18 (3.94)
18	1	9.29 (3.48)	10.59 (3.50)	13.74 (3.24)	13.20 (3.29)	3.48 (1.75)	6.54 (3.18)
	2	7.33 (0.09)	12.93 (0.74)	11.88 (0.13)	15.26 (0.40)	1.04 (0.32)	6.41 (0.92)
	3	10.92 (0.15)	7.50 (0.30)	14.50 (0.15)	9.67 (0.22)	1.31 (0.28)	6.06 (0.35)
	4	8.34 (0.24)	12.70 (1.23)	14.35 (0.18)	15.46 (0.27)	2.21 (0.27)	8.42 (2.03)
30	1	5.40 (3.68)	5.30 (1.48)	11.46 (3.61)	15.48 (6.54)	4.47 (2.44)	13.97 (6.88)
	2	2.93 (3.31)	5.44 (3.01)	13.97 (1.55)	13.00 (2.18)	9.46 (1.54)	10.88 (2.19)
	3	7.51 (1.52)	−0.76 (0.36)	13.18 (1.87)	15.39 (0.63)	6.09 (3.80)	15.08 (0.48)
	4	2.92 (1.52)	2.93 (1.16)	14.25 (0.31)	11.74 (4.48)	9.73 (0.85)	11.02 (5.06)

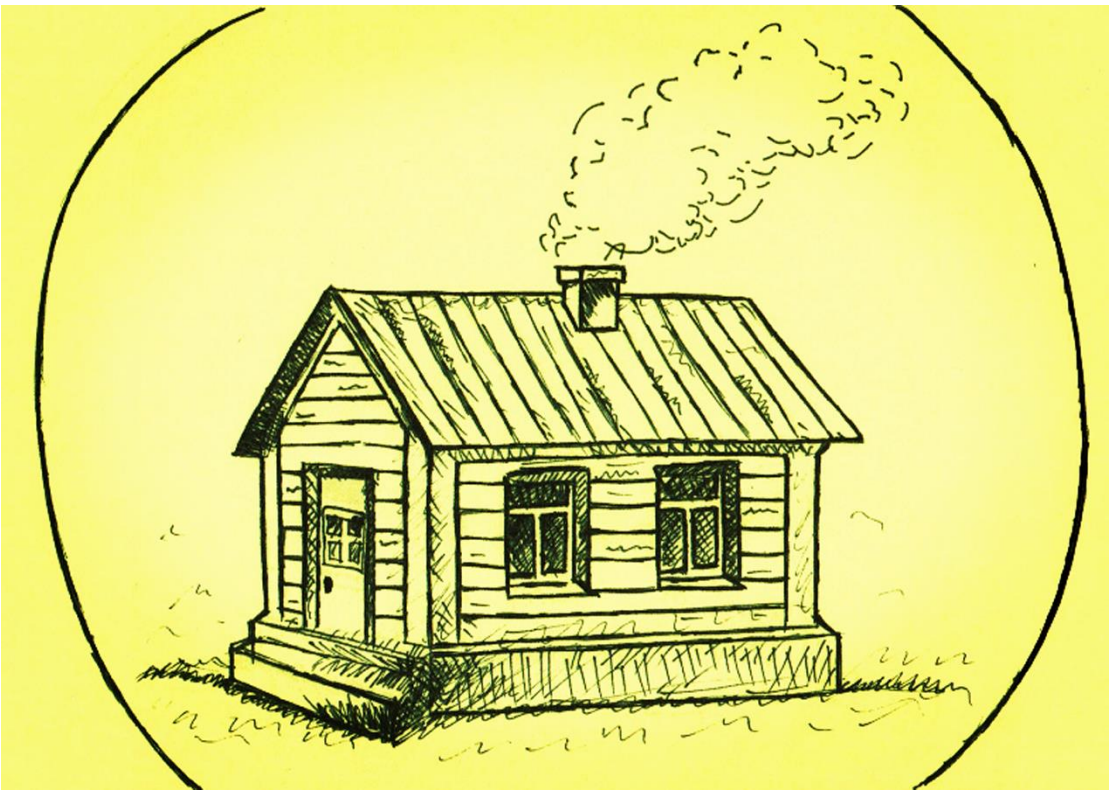
3.4 Conclusions

Changes in the surface of *C. lanceolata* were observed and analyzed under natural conditions. The variation in intrinsic weathering behavior was determined by physical and anatomical research. The color change of the surface of the wood was evident from the beginning of exposure. The observed structural changes were not detected until one week of exposure. However, the surface microstructure of *C. lanceolata* was seriously damaged after one month of exposure.

The color change of the surface of *C. lanceolata* was inhibited by extractives at the beginning of exposure. Nevertheless, with the prolongation of exposure time, it was found that the weathering resistance of heartwood was still lower than that of sapwood. Weathering behavior of *C. lanceolata* was enhanced from bottom to top in the axial direction. This study indicated that the photodegradation of wood decreased with an increase in the density. The high-density timber should be selected to mitigate the effects of weathering on wood.

Understanding the weathering behavior of wood provides reference for weatherproofing pre-treatment. Obtaining the weathering behavior of wood can result in a more effective use of wood, fully leveraging the advantages of the wood itself and maximally improving the efficiency of wood. Considering the depletion of forest resources, the efficient use of wood also protects the environment.

CHAPTER 4 Wood Surface Changes of Heat-Treated *Cunninghamia lanceolata* Following Natural Weathering



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4.1 Abstract

To quickly clarify the effect of heat treatment on weatherability of *C. lanceolata*, we investigated the surface degradation under natural exposure. A comparison between heat-treated and untreated samples was taken based on surface color changes and structural decay at each interval. Over four weeks of natural exposure, multiple measurements were carried out. Results show that color change decreased in the order of 220 ◦C heat-treated > untreated > 190 ◦C heat-treated. The results also indicate that the wood surface color stability was improved via the proper temperature of thermal modification. Low vacuum scanning electron microscopy (LVSEM) results expressed that thermal modification itself had caused shrinking in the wood surface structure. From the beginning of the weathering process, the heat treatment affected the surface structural stability. After natural exposure, the degree of wood structure decay followed the pattern 220 ◦C heat-treated > 190 ◦C heat-treated > untreated. Therefore, when considering the impact on the structure, thermal modification treatment as a protective measure to prevent weathering was not an ideal approach and requires further improvement.

Keywords: natural weathering; heat-treated; color change; wood anatomical; *Cunninghamia lanceolata*

4.2 Introduction

In recent years, the wood protection industry has been paying greater attention to environmentally friendly substitutes for traditional wood protection treatments. One existing environmentally conscious method is the thermal modification of wood. Modified wood does not impregnate the material with any harmful substances or chemicals and the finished material does not produce environmental pollution. In the heat treatment process, the wood is heated to high temperatures, ranging from 160 ◦C to 260 ◦C, for various standing times based on the species and the desired material properties (Alfred et al. 1946, Alfred 1956, Esteves et al. 2009, Militz 2002). Thermal modification offers particular benefits. In general, it reduces the equilibrium moisture content, improves hydrophobicity, enhances dimensional stability, maintains uniform wood color, and offers improved protection, especially against damage caused by micro-organisms and insects. However, brittleness, cracking, and other forms of mechanical strength loss are the main disadvantages of heat-treated wood (Alfred et al. 1946, Esteves et al. 2009, Kocaefe et al. 2008). Thermally modified wood has many applications for exterior structures, including terraces, fences, decks, cladding, garden furniture, doors, and windows; as well as interior uses, e.g., decorative panels, parquet, kitchen furniture, and saunas (Esteves et al. 2009, Bengtsson et al. 2002, Syrjänen et al. 2000).

Weathering is the general term used to refer to the slow degradation of materials when exposed to the weather. It can be influenced by several factors, including sunlight, moisture, heat/cold, wind, air pollutants, and biological agents (Williams 2005). Weathering of wood surfaces can cause color, chemical, physical, mechanical, and microscopic changes. These changes occur in the wood surface at a depth of 0.05–2.5 mm during the initial weathering period (William et al. 1984).

Earlier research generally examined the resistance of heat-modified wood to artificial weather (Ayadi et al. 2003, Deka et al. 2008, Huang et al. 2012, Yildiz et al.

2013, Todaro et al. 2015, Xing et al. 2015, Shen et al. 2016). Heat-treated wood exhibits high physical characteristics and low mechanical properties during artificial weathering. Artificial weathering tests are generally considered to be a simulation of outdoor conditions, but this method includes only UV light and moisture cycles. There are many other degradation factors in the natural environment, such as microbes, air pollutants, chemicals, and biological agents (Williams 2005). Therefore, and artificial weathering experiment cannot fully substitute for a study of natural weathering, and it is still necessary to test the service life of wood. Research of natural weathering always takes many years. In fact, the surface changes of weathering characteristics begin from the moment the wood is exposed to the outdoor environment. It has been reported that the surface characteristics of wood can change significantly during a short exposure period Evans et al. 1996). Therefore, surface change analysis is a method that can evaluate the weatherability of wood over a short period of time.

The purpose of this study is to clarify the effect of heat treatment on the weatherability of *C. lanceolata* wood. We conducted an outdoor exposure experiment for one month and examined the anatomical and physical changes of wood surface. In order to attain these objectives, some techniques and methods for the study of wood surfaces were used such as a colorimeter for physical color changes and low vacuum scanning electron microscopy (LVSEM) for anatomical changes. These analytical tools provided accurate insight into the degradation process, which allowed a comparison between heat-treated and untreated *C. lanceolata* exposed to natural conditions.

4.3 Materials and Methods

4.3.1 Preparation of Wood Samples

All the samples used in this study were taken from *C. lanceolata* (Li et al.1999). Samples were obtained from sapwood straight off the grain, and each was free of knots and visible defects. Samples were 10 (R) × 10 (T) × 10 (L) mm in size. Under drying conditions, three parts of the samples were cut with a hammer microtome. Lumber was heat-treated at 190 ◦C and 220 ◦C for 120 min, respectively, under steam. This range was chosen because 220 ◦C is a significant critical point for the heat treatment of *C. lanceolata* (Cao et al. 2012). From previous studies of Chinese fir (Cheng 2007), heat treatment at 190 ◦C and 220 ◦C was determined to be optimal temperatures for strength and corrosion resistance, respectively. Timbers were dried to a moisture content of 8% prior to the steam-heat treatments. About 4% moisture content was achieved after the steam-heat treatments. Samples were classified into three groups as follows: (1) untreated controls, (2) 190 ◦C heat treatment, and (3) 220 ◦C heat treatment.

4.3.2 Natural Weathering Conditions

Untreated and heat-treated *C. lanceolata* samples were placed in an outdoor environment for four weeks. The experiment was conducted during the summer season of 2018 in Fukuoka, Japan. The statistics mean temperature, humidity, duration of sunshine, total rainfall and wind speed were 30.01 ± 1.41 ◦C, 67.81% ± 6.31%, 9.13 ± 3.57 h, 1.68 mm, and 2.92 ± 0.80 m/s, respectively. They were orientated in a south-facing position at 45◦ relative to the horizontal (latitude 33◦ north) according to JIS K 5600-7-6 (Japan Meteorological Agency 2018). After one day of exposure, all the specimens were retrieved from the weathering racks, and measurements were taken in a laboratory, after which they were put back on the weathering racks. This was repeated after 2, 4, 7, 14, 21, and 28 days (Kataoka et al. 2009). On each occasion, a puff of nitrogen was used to gently clear the surface of dust.

4.3.3 Color Measurements

Color measurements were used to evaluate the degree of color change on the sample surfaces after each period of natural weathering (Kataoka et al. 2009). There were 10 replicates for each treatment group. A mathematical average was established based on 30 measurements for every data point of color measurement. For each sample, the color coordinates L*, a*, and b* were established both before and after exposure to weather. A handy colorimeter (Model NR-3000, Nippon Denshoku, Tokyo, Japan) was used to measure the color change, with a D65 standard illuminant and the 2◦ standard observer. The color difference values of ΔC*, ΔE*, and ΔH* were determined before and after the natural conditions. C* indicates chroma, while ΔC* is the chroma difference. The parameter ΔE* indicates the total difference value. ΔH* is the difference in hue (Robertson 1977, Tolvaj et al. 1995). Average values and standard deviation were computed for each sample. These parameters were then employed to establish ΔC*, ΔE*, and ΔH* based on the following formulae:

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \quad (1)$$

$$\Delta C^* = C^* - C_o^* \quad (2)$$

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (3)$$

$$\Delta H^* = [(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2} \quad (4)$$

Positive values of ΔC* indicate greater vividness, whereas a negative value indicates a more faded hue in comparison to the initial color. A low ΔE* indicates that the color was not altered very much or remained the same, while a high value indicates obvious color change. ΔH* records the extent of the hue change.

4.3.4 Statistical Analysis

By statistical analysis of the color data before and after natural weathering, the color difference values of different exposure times did not conform to normal distribution. The rank sum test method of paired samples was selected in this experiment. With the change of exposure time, the color difference of 190 ◦C and 220 ◦C heat-treated wood was compared separately with that of untreated samples. The measurement index is the color difference values of ΔC*, ΔE*, and ΔH*, which were the quantitative data of the paired design. The rank of the contrast difference was reported in the results. The results of the Wilcoxon signed ranks test indicated the Z value, the approximate method was used to calculate the *p* value, and the statistical significance of the difference was determined.

4.3.5 Low-Vacuum Scanning Electron Microscopy (LVSEM)

During the natural weathering experiment, samples that had no coating were observed via low-vacuum scanning electron microscopy (LV-SEM, Model JSM-5600LV, JEOL, Tokyo, Japan). The microscopy conditions were as follows: a voltage of 15 kV, a pressure of approximately 10–30 Pa, and a working distance of 10–20 mm. This LVSEM method was deployed over the exact same area of wood surface before and after exposure. LVSEM was a valuable tool to observe the anatomical changes in the process of weathering (Hatae et al. 2012a, 2012b).

4.4 Results

4.4.1 Discoloration of Wood Surfaces

Wood absorbs light, and polymeric compounds inside wood interact with photons. These factors lead to the deterioration and discoloration of wood. When wood is exposed to natural conditions, other factors such as moisture and microorganism growth also contribute to the degradation. The color of the exposed wood is influenced by light radiation, rain water, and temperature. UV light causes particularly remarkable color changes (Tolvaj 1995, Pandey 2005, Mitsui et al. 2005, Miklecic et al. 2011). Color stability is an important parameter among the physical properties of wood.

After heat treatment, the color exhibited a notable change, and the colors visible to the naked eye became darker. L* (lightness) decreased, while a* (redness) increased. Different temperatures had effects on the color of wood. B* (yellowness) and C* (chroma) increased after 190 ◦C heat treatment, while these variables decreased after 220 ◦C heat treatment. These changes might be due to hydroxyl groups that were oxidized to carbonyl groups and carboxyl groups during heat treatment. If this is the case, then the wood color was darkened because the carbonyl groups belong to chromophric groups and the carboxyl groups to auxochromic groups (Funaoka 1990).

Figure 4.1 shows the color modifications (L*, a*, b*, and c*) of untreated and heat-treated wood surfaces while exposed to natural conditions. Increases in a* (redness) were observed with the increase in exposure time during the first stages. Redness of heat-treated samples underwent an especially noticeable increase after the first weathering day. However, a slow increase in redness was also shown during the first 4 exposure days for untreated samples. After the first 4 days, the value of a* decreased quickly for both untreated and heat-treated wood. Increases in b* (yellowness) and c* (chroma) were observed with increases in the number of natural weathering days. In particular, b* and c* exhibited rapid increases during the first week. Nevertheless, a slow increase in these values was also shown in the natural weathering experiment after

the first week. This implies that the first week is a critical period for changes in yellow and intense chroma during the natural weathering. The L* (lightness) value of untreated wood demonstrated a decrease in each treatment, but the L* values increased as the number of days increased for wood that received heat treatment at 190 ◦C and 220 ◦C. As time increased during the first week, the value of L* changed rapidly. After one week, however, the value of L* changed incrementally. The darkening of untreated wood might be caused by high temperature inducing the migration of extractives to the wood surface. Several previous studies have reported similar results (Deka et al. 2008, Huang et al. 2012, Masanori et al. 2004, Dubey et al. 2010, Temiz et al. 2006). The surface of heat-treated wood became lighter during weathering as the extractives were degraded and removed. This lightening was mainly due to the photodegradation of lignin (Huang et al. 2013).

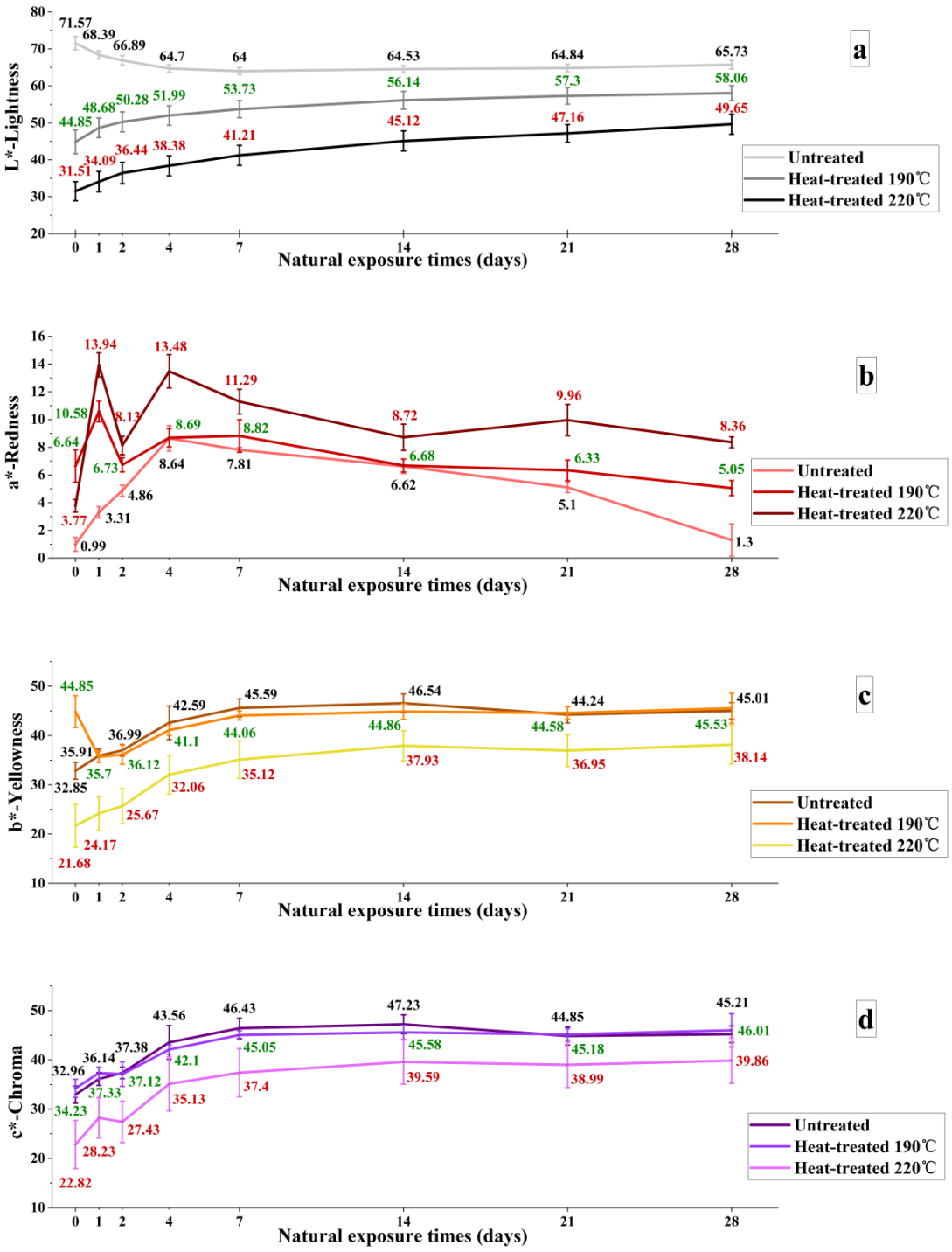


Figure 4.1 Color modifications for each of the four weeks of natural exposure:

(**a**) Lightness L*; (**b**) redness a*; (**c**) yellowness b*; (**d**) chroma c*

Figure 4.2 shows the effect of natural exposure on ΔC*, ΔE*, and ΔH*, revealing the color changes as a result of the effects of natural weathering on wood samples. The ΔC* (chroma difference) values in untreated and in heat-treated wood increased significantly in the first seven days, and the values then stabilized after the first week. The ΔC* value for 190 ◦C heat-treated wood was lower than other treatments. This result indicates that 190 ◦C heat treatment could attenuate the chroma difference during the natural weathering process. The values of ΔH* (hue difference) exhibited insignificant changes during the four weeks of the experiment for both untreated and heat-treated wood (Figure 4.2c). Meanwhile, ΔE* (total color difference) values in untreated wood increased quickly over the initial seven-day period, and the values then started decreasing after two weeks. However, this phenomenon was not found in heat-treated wood. This implies that untreated and heat-treated samples exhibited different color change responses during the four weeks of natural weathering.

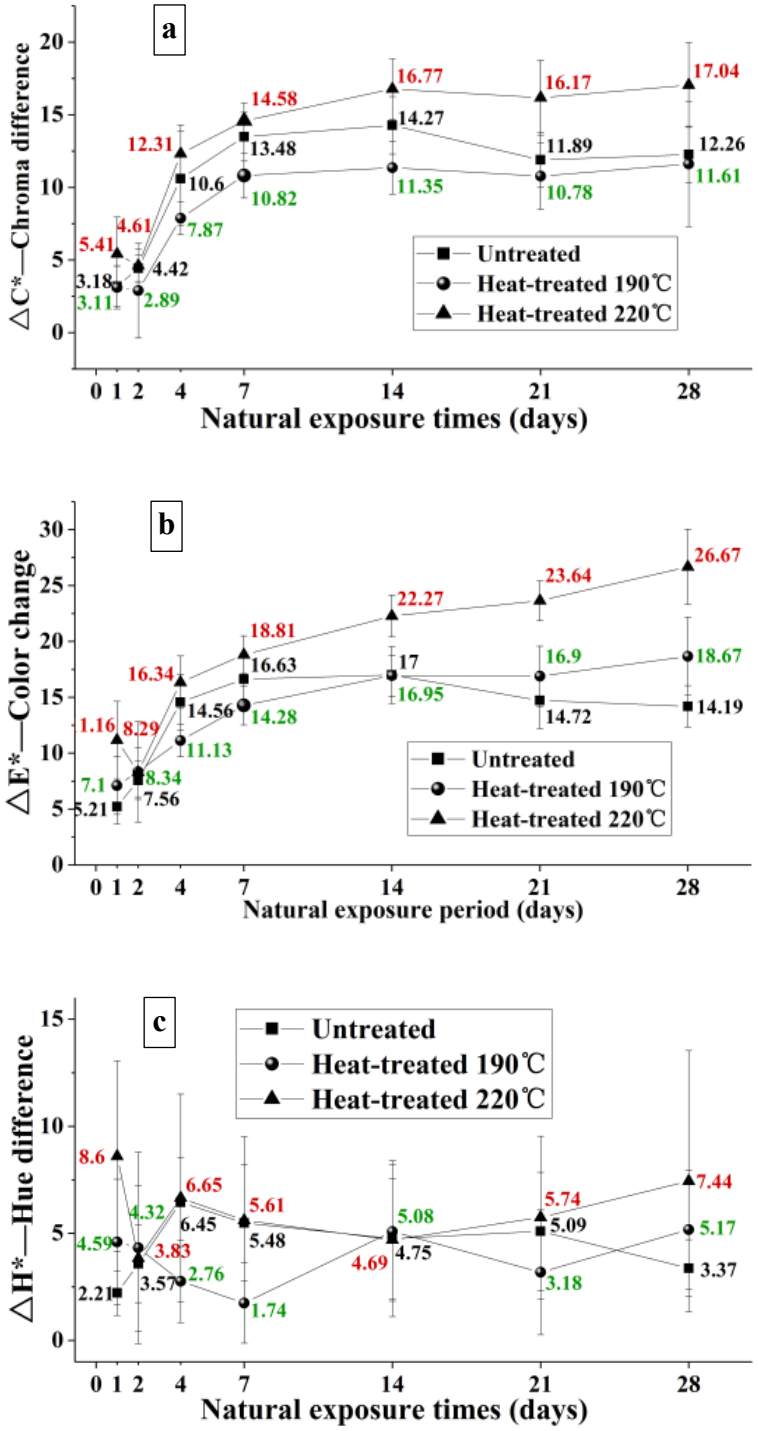


Figure 4.2 Color changes of wood samples subjected to natural conditions: (**a**) Chroma difference Δc*; (**b**) color change ΔE*; (**c**) hue difference ΔH*.

Wilcoxon signed ranks test statistics demonstrated significant differences in ΔC*, ΔE*, and ΔH* values during the four weeks of natural exposure for the untreated, 190 ◦C heat-treated, and 220 ◦C heat-treated wood samples (Table 4.1). The results illustrated that the surface chroma exhibited a significant negative difference for both the 190 ◦C heat-treated and untreated in the initial stage of natural weathering (Table 4.2). The 190 ◦C heat treatment clearly promoted the stability of chromaticity. The same results were also obtained for ΔE* (total color difference value) and ΔH* (hue difference), but the differences were not so significant. However, the 220 ◦C heat-treated wood exhibited a significant positive difference in ΔC*, ΔE*, and ΔH* when compared to untreated wood (Table 4.2). This shows that 220 ◦C heat treatment could not stabilize the color during the process of weathering. On the contrary, this treatment brings about greater color change (Table 4.1).

Table 4.1 Ranks heat-treated–untreated.

			N	Mean Rank	Sum of Ranks
ΔC*	190 °C heat-treated–untreated	Negative ranks	48 [a]	37.11	1781.50
		Positive ranks	20 [b]	28.23	564.50
		Ties	0 [c]		
		Total	68		
	220 °C heat-treated–untreated	Negative ranks	17 [a]	22.12	376.00
		Positive ranks	53 [b]	39.79	2109.00
		Ties	0 [c]		
		Total	70		
ΔE*	190 °C heat-treated–untreated	Negative ranks	39 [a]	30.74	1199.00
		Positive ranks	29 [b]	39.55	1147.00
		Ties	0 [c]		
		Total	68		
	220 °C heat-treated–untreated	Negative ranks	4 [a]	14.50	203.00
		Positive ranks	56 [b]	40.75	2282.00
		Ties	0 [c]		
		Total	70		
ΔH*	190 °C heat-treated–untreated	Negative ranks	41 [a]	35.30	1447.50
		Positive ranks	27 [b]	33.28	898.50
		Ties	0 [c]		
		Total	68		
	220 °C heat-treated–untreated	Negative ranks	28 [a]	30.20	845.50
		Positive ranks	42 [b]	39.04	1639.50
		Ties	0 [c]		
		Total	70		

[a] Heat-treated < untreated; [b] Heat-treated>untreated; [c] Heat-treated = untreated.

Table 4.2 Test statistics; a heat-treated–untreated

	ΔC*		ΔE*		ΔH*	
	190 °C	220 °C	190 °C	220 °C	190 °C	220 °C
Z	−3.718 [b]	−5.071 [b]	−0.159 [b]	−6.083 [b]	−1.677 [b]	−2.323 [b]
Asymp. Sig. (2-talled)	**	**	0.874	**	0.093	*

[a] Wilcoxon signed ranks test; [b] Based on negative ranks. * Statistically significant $p < 0.05$; ** Statistically significant $p < 0.01$.

Other researchers (Cheng et al. 2016, Xing et al. 2014) reported that cellulose remained relatively stable after heat treatment of *C. lanceolata*. In hemicelluloses, the acetyl group was decomposed from molecular chains to acetic acid and degraded pyranose. A cross-linking occurrence had been formed among the aromatic units in the lignin. The observed that higher heat treatment temperatures intensified the reaction (Cao et al. 2012). In the present study, there are two potential reasons for the favorable color stability under natural weathering of wood heat-treated at 190 ◦C. First, the heat treatment temperature of 190 ◦C may not have been enough to greatly change the chemical composition of wood because hemicellulose degradation was less 3% (Cheng et al. 2016). Second, color deepening after heat treatment could inhibit the color change to a certain extent (Svetlana et al. 2012, Hyvärinen et al. 2015). As a result, the color change of wood during natural exposure was weakened and the color stability was improved after 190 ◦C heat treatment. The relative content of lignin in wood was significantly increased after heat treatment at 220 ◦C because of the degradation of hemicellulose (Cao et al. 2012, Cheng et al. 2016). The most important change in the process of weathering was the decomposition of lignin (Tolvaj et al. 1995, Pandey 2005, Tolvaj et al. 2003, Tolvaj et al. 2008, Preklet et al. 2012, Calienno et al. 2014). This directly results in the aggravation of weathering, and the color change was very significant. Therefore, selecting the appropriate thermal modification temperature played a substantial role in color stability during the weathering process.

4.4.2 Wood Structure Changes

The changes of wood surface structure accompany other physical changes taking place during the natural weathering. Heat treatment changes the characteristics of wood, including microscopic structural changes. In this study, low vacuum scanning electron microscopy (LVSEM) was used to investigate the wood structure degradation of heat-treated *C. lanceolata* subjected to natural exposure. Both heat-treated and untreated wood surfaces were surveyed for comparison. LVSEM analysis of the three sections of heat-treated *C. lanceolata* sapwood showed obvious microscopic structural changes that took place during the short-term exposure to conditions (Figures 4.3 and 4.4). It was found that microstructure did not change in the first two days of natural weathering, until after four days had a little change (as shown in Figure 4.4g).

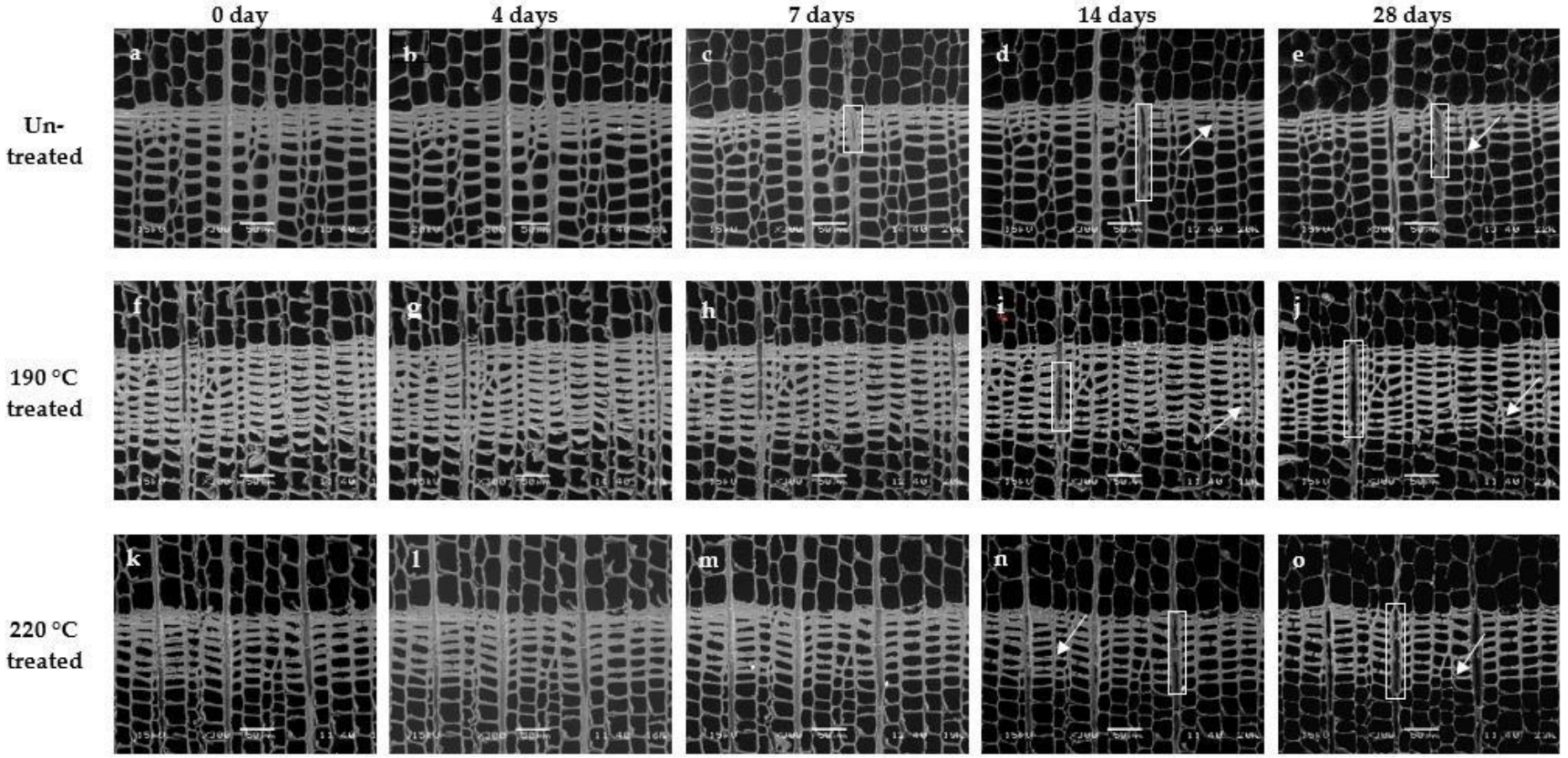


Figure 4.3 Scanning electron micrographs of cross sections of untreated and heat-treated wood before and after natural weathering. The arrows and squares in the figures showed that the areas of significant change in microstructure were affected by weathering.

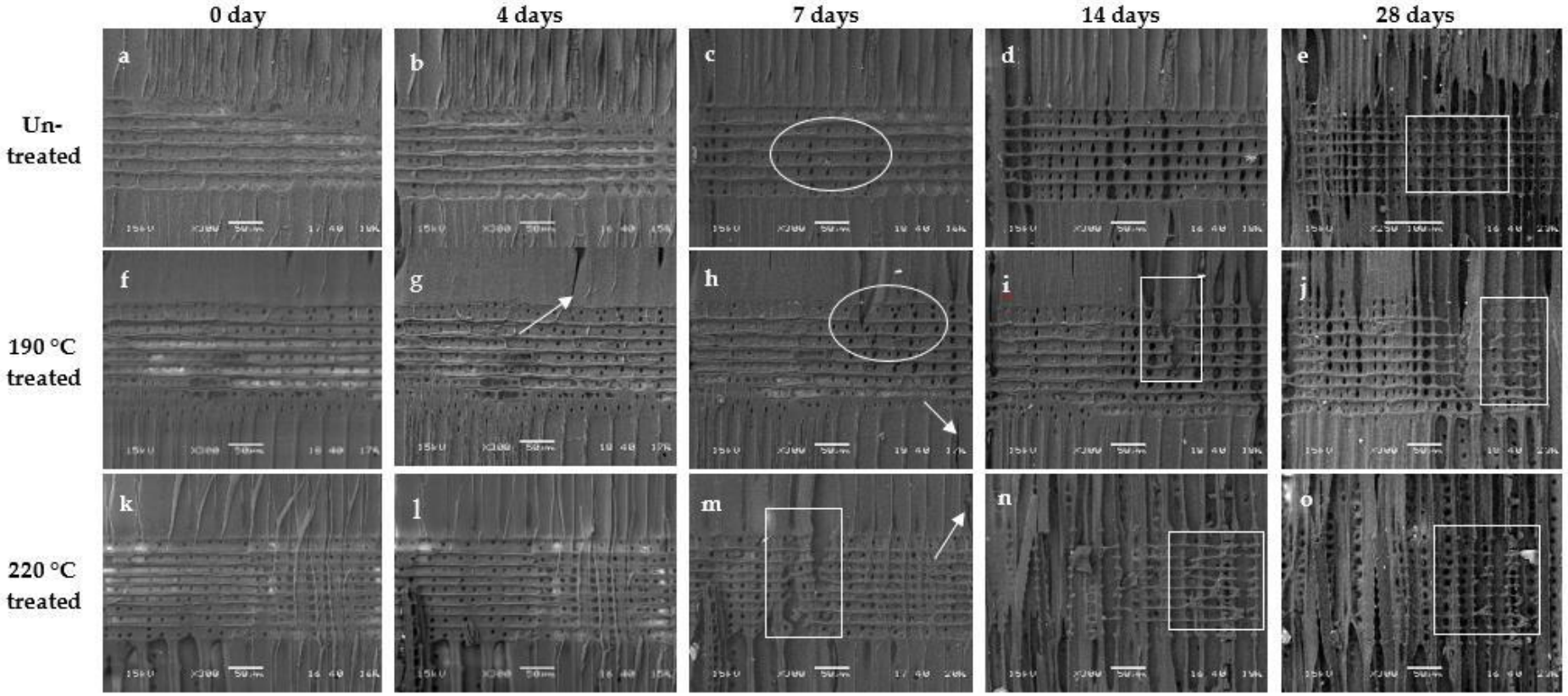


Figure 4.4 Scanning electron micrographs of radial sections of untreated and heat-treated wood before and after natural weathering. The arrows and squares in the figures showed that the areas of significant change in microstructure were affected by weathering.

4.4.2.1 Cell Wall

As shown in Figure 4.3a, f, k the microstructure of the heat-treated wood was rougher than the microstructure of untreated wood. Heat treatment caused the cell wall to become slightly plasticized (Boonstra et al. 2006). The surface of the heat-treated *C. lanceolata* wood was more brittle than the surface of untreated wood. In contrast, the 220 ◦C heat treatment had greater effects than the 190 ◦C heat treatment. After four weeks of natural weathering, the middle lamella and primary cell wall had substantially disappeared (as shown by the arrows in Figure 4.3e, j, o). Compared with the unexposed condition, the secondary cell wall became obviously thinner. The degradation of the secondary cell wall in heat-treated wood was more severe than untreated wood under natural weathering conditions. The comparison between the two heat treatment groups found that higher heat treatment temperatures produced more severe weathering erosion of the secondary cell wall (Figure 4.3).

The S1 layer comprises 30.0% cellulose, 51.7% lignin, and 18.3% hemicellulose. The S2 layer comprises 54.3% cellulose, 15.1% lignin, and 30.6% hemicelluloses. The S3 layer is composed of 13% cellulose, no or only negligible amounts of lignin, and 87% hemicelluloses (Rowell et al. 2005). The lignin content in wood exposed for four weeks is somewhat lower than the content in wood exposed for seven days. Compared with the untreated wood, the heat treatment caused significant degradation of hemicellulose and cellulose in the cell wall. Therefore, the lignin percentage was relatively increased. Chemical composition changes caused differences in the structure. As a result, the change in the material from exposure was more significant in heat treatment groups. However, there is a rupture phenomenon in the weathering stage due to the high level of lignin in the cell wall of the wood exposure for seven days. Previous studies on the heat treatment of *C. lanceolata* showed that chemical changes increased with high temperature. The degree of wood plasticization increased with the proportion of hemicellulose and cellulose (Syrjänen et al. 2000, Cao et al. 2012). The results of

this experiment are consistent with previous research conclusions that reported that heat treatment produced microstructural changes (Huang et al. 2012).

In the case of *C. lanceolata*, the untreated and the heat-treated wood tended to show degradation in the primary cell wall and middle lamella when subjected to natural weathering after two weeks (as shown by the arrows in Figure 4.3d, i, n). According to the literature (Rowell et al. 2005), the primary cell wall and middle lamella comprised primarily lignin (84%), a smaller percentage of hemicelluloses (13.3%), and a very small percentage of cellulose (0.7%). The disappearance of the primary cell wall and lamella in wood after four weeks of weathering evidenced that the most photosensitive component of the cell wall was lignin. This conclusion conformed to previous studies (Huang et al. 2012). The lignin content in the cell walls of the heat-treated *C. lanceolata* was much higher than that of the untreated control group, and higher heat treatment temperatures produced higher proportions of lignin in the cell wall (Cao et al. 2012, Rowell et al. 2005). The cell wall lignin content exhibited the following pattern: 220 ◦C treated > 190 ◦C treated > untreated. Structures with high lignin content were more seriously eroded during weathering due to the photodegradation of lignin. The degree of cell wall damage after weathering followed the pattern: 220 ◦C treated > 190 ◦C treated > untreated.

4.4.2.2 Rays

Figure 4.3a, f, k show that the heat treatment apparently did not alter the microstructure of the wood rays. After natural weathering over 28 days, ray parenchyma cells exhibited a much higher the degree of degradation in the heat treatment groups and untreated groups than surrounding tracheids (as shown by the square area in Figure 4.3e, j, o). It is well known that parenchyma cells only possess very thin primary cell walls and no secondary walls. The chemical constituents of these cell walls are mostly lignin (Todaro et al. 2015). After heat treatment, these cell walls are still mainly composed of lignin. The attenuation of the cell wall in the parenchyma cells during the weathering process was obvious. This provides more evidence that the photosensitivity of lignin was particularly prominent.

4.4.2.3 Cross-Field

SEM pictures of the cross-field structure on the radial section of untreated and heat-treated samples displayed certain differences (Figure 4.4). Serious structural damage was found at the cross-field after heat treatment at 220 ◦C (shown in Figure 4.4m). Longer exposure times produced the more obvious damage. After 28 days of weathering, the cell walls of the ray parenchyma at the cross-field position were significantly degraded (as shown by the square area in Figure 4.4e, j, o). Compared with the thickness of cross-field tracheid walls after weathering, the degradation of ray parenchyma cells was obvious. These cells only possess primary walls and do not contain secondary walls. Therefore, their main components were lignin (Todaro et al. 2015, Rowell et al. 2005), and lignin was highly degraded during weathering. The degradation degree of tracheid cell walls also increased with higher heat treatment temperatures.

In SEM micrographs of the cross-field pits of *C. lanceolata*, it can be seen that the pits did not suffer damage due to the heat treatment process (Figure 4.4f, k). The edges of the bordered pits were destroyed after 1 week of weathering and cracked along the

direction of the microfibril (as shown by the circle area in Figure 4.4c, h, m). Higher heat treatment temperatures produced higher plasticity. During the process of weathering, cracking was more likely to occur under the influence of shrinkage and swelling.

4.4.2.4 Tracheids

Micrographs of the radial surface of untreated and heat-treated wood demonstrated that the natural weathering process caused degradation of the wood surface. After only a week, severe longitudinal micro-cracks appeared on the tangential surface tracheids of the heat-treated wood (as shown by the arrows in Figure 4.4h, m). Cellulose is responsible for wood strength, hemicelluloses and lignin compose the matrix system in wood, and lignin provides wood with rigidity or stiffness. During the process of weathering, the change of humidity and the loss of lignin in the secondary cell wall caused serious surface shrinkage and made the wood crack more easily. After heat treatment, plasticization exacerbated the cracking.

4.5 Discussion

In summary, it can be seen that the more serious deterioration during the natural weathering process was caused by the anatomical position of high lignin content. Lignin was always the most sensitive chemical component in weathering, and this is consistent with the results of previous studies (Tolvaj et al. 1995, Pandey 2005, Tolvaj et al. 2003, Pandey et al. 2008, Preklet et al. 2012, Calienno et al. 2014). Relative lignin content depended more on the degradation of hemicellulose at higher treatment temperatures (Funaoka et al. 1990, Cheng et al. 2016). The more obvious the decay phenomenon happened in the high lignin content anatomical position under natural exposure. We conclude that heat treatment of wood could not improve structural stability; on the contrary, it would aggravate the decline of the anatomical structural structure. Both 190 ◦C and 220 ◦C heat treatments accelerated the aging phenomenon, and these results differ only in degree. These trends were contrary to the results of color stability.

Heat-treated wood, considered comprehensively, can enhance the dimensional stability of wood, maintain uniform wood color, and, most importantly, prevent degradation caused by microorganisms and insects (Alfred et al. 1946, Esteves et al. 2009, Kocaefe et al. 2008). These advantages play a very positive role in the natural weathering of wood. In particular, reducing the damage caused by microorganisms and insects greatly improves the degradation resistance of the wood itself, and it mitigates the effects of natural weathering caused by decay. However, because heat treatment reduces the mechanical strength and structural stability of wood, heat treatment as a means of wood weatherproofing should be comprehensively evaluated first. In the process of heat treatment, the changes of mechanical strength and structural stability should be considered and serve as the focus of future research. Making full use of the advantages of improving corrosion resistance and reducing the loss of mechanical strength and structural stability, heat treatment technology is better applied to the environmentally friendly modification of wood weathering prevention, and the utilization rate of wood is thus improved.

4.6 Conclusions

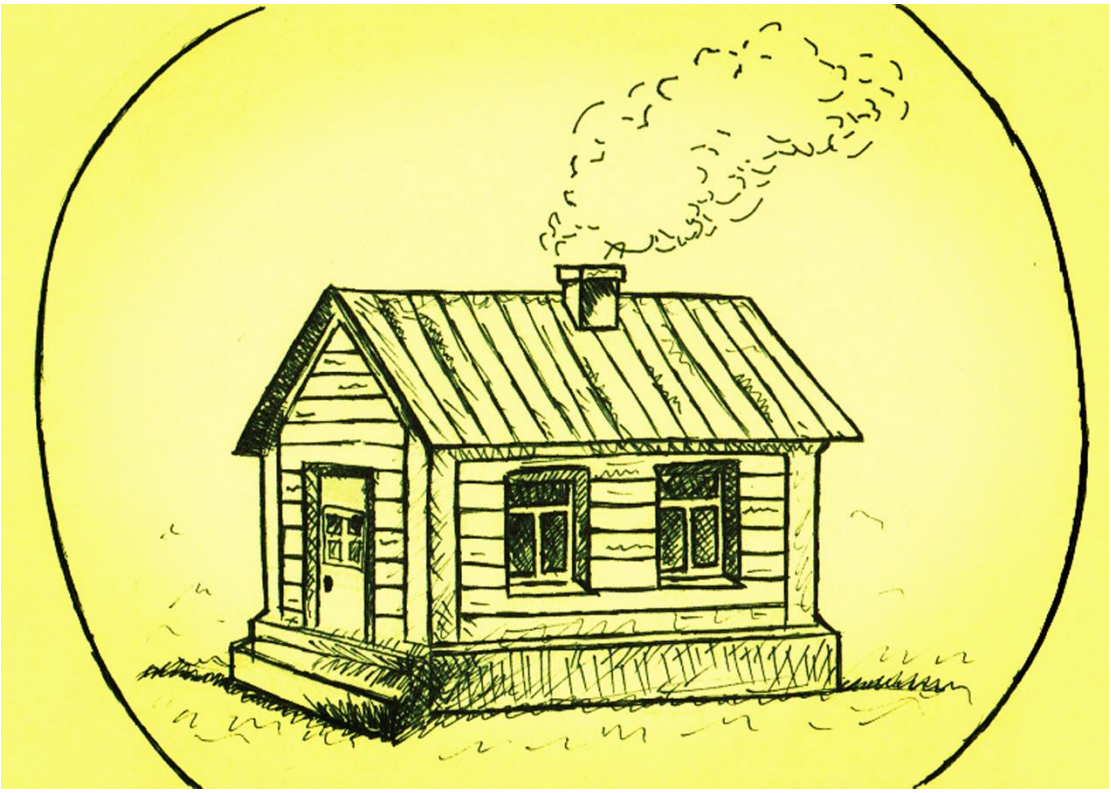
Heat-treated and untreated *C. lanceolate* samples were exposed to natural conditions for one month. The physical and anatomical changes were examined on wood surfaces by different analysis methods.

After 190 ◦C heat treatment, the color change of the *C. lanceolata* surface was significantly restrained in the process of natural weathering. Heat treatment played a positive role in maintaining the physical properties of wood.

The LVSEM study indicated that heat treatment aggravated the degradation of the wood structure in *C. lanceolata* subjected to natural conditions. Thermal modification was not conducive to the maintenance of structural stability.

The effect of heat treatment on the weatherability of *C. lanceolata* wood was beneficial for aesthetic properties and harmful for structural properties. If heat treatment is deployed as an anti-weathering treatment method, practitioners should comprehensively consider the advantages and disadvantages of thermally modified wood.

CHAPTER 5 Effectiveness of low-molecular weight phenolic resin for improving the durability of *Cunninghamia lanceolata* (Lamb.) Hook.



5.1 Abstract

To elucidate the effect of low molecular weight phenolic (LMWP) resin treatment on the weathering resistance of *C. lanceolata*, we investigated the surface degradation of wood with natural exposure. The resin-treated and untreated samples were compared according to the surface color changes and the structural decay of each time period. Periodic observations were performed with the surrounding natural exposure. The results showed that the color stability of the wood surface was improved for short-term (one week) weathering after resin treatment. The low-vacuum scanning electron microscopy (LVSEM) results showed that the resin treatment reinforced the wood surface structure. The resin treatment improved the stability of the surface structure from the beginning of the weathering process; therefore, LMWP resin impregnation used as a protective measure to prevent weathering was an ideal method.

Keywords: *Cunninghamia lanceolata*; low-molecular phenolic resin; weathering; wood surface changes; durability

5.2 Introduction

Since environmental issues have become widely discussed around the world, key phrases such as environmental protection and sustainable development are well known to the public. In order to relieve environmental pressure and protect forest resources, the full utilization of wood as a renewable resource is also an environmental conservation practice (Geiser 2001, Finlay 2004). Since the middle of the 20th century, the modification of wood has been a matter of wide concern (Hill 2006). Traditional wood protection treatments usually involve the impregnation of preparations with adverse environmental effects on wood (Henningsson and Carlsson, 1984). However, the negative impacts of these methods on the environment may limit their future applications. It was clear from the evolution of the European wood market in recent years that the use of biocides in wood treatment has become increasingly limited due to environmental problems. This brings new opportunities for the development of environmentally friendly modified preparations (Schultz et al. 2007). A number of references and books have presented the methods for modifying wood and industrial applications of the new materials have been developed from wood modifications (Rowell 2005, Hill 2006).

From a chemical point of view, wood is a natural composite material consisting of cellulose, hemicellulose and lignin, and a small amount of low-molecular weight compounds, i.e., extracts (Rowell 2005). The chemical structure of these components directly affects the chemical reactivity of wood. The main purpose of wood modification is to reduce the hygroscopicity of wood, improve the dimensional stability of wood, and improve the biodegradability of wood (Hill 2006). In order to achieve these objectives, the following countermeasures are used. First, the hydroxyl groups of wood cell wall polymers are modified by esterification, amination, or alkylation. Second, after in situ polymerization, the polymerizable monomers or resins are impregnated into the wood structures to form wood polymer composites. In reactions involving wood hydroxyl modification, stability is due to the reduction of free sites

capable of binding water with hydrogen bonding, but also due to the expansion effect of groups grafted on wood. For the case of wood polymer composites, stability is either due to the ability of a polymer to fill a cavity, which reduces accessibility to water and microorganisms, or due to the cross-linking of wood components (Gérardin 2016). Chemically or thermally modified wood constitutes a valuable alternative to traditional preservation methods, and it will become more important in different applications in the future. At present, only a few chemical modification methods have achieved industrial scale development, but their utilization will also become more and more important and may continue to increase in the future. The improvement in durability depends on the nature of the modified materials (Hill 2006). The thermosetting resin is cured at high temperature to keep the cell wall in a state of permanent expansion. Thermosetting resins have been used to develop some wood polymer composites with commercial applications (Stamm & Seborg 1962).

C. lanceolata is one of the most widely used tree species in China. In many traditional wooden houses and buildings in southern China, the wood products of *C. lanceolata* have been used outdoors for many years and these products have received wide attention (Fu et al. 1999, Jøker 2000, Orwa et al. 2009). For this outdoor application, *C. lanceolata* needs to be modified to prevent severe weathering. The purpose of this study was to clarify the effect of low molecular weight phenolic (LMWP) resin impregnation on the weathering resistance of *C. lanceolata*. The changes of the surface color and the anatomic structure of untreated *C. lanceolata* and treated LMWP resin were studied. To achieve these objectives, conventional physical color change measurement and low-vacuum scanning electron microscopy (LVSEM) observations were used to analyze the changes of the wood surfaces. The differences between untreated and resin-treated wood with natural exposure were also investigated.

5.3 Material and Methods

5.3.1 Materials

The samples used in this study were taken from *C. lanceolata* (Fu et al.1999). The sapwood and heartwood samples were cut from the tree at positions 1 m above the ground. Each sample had a straight texture, was free of knots, and had no visible defects. Under the air-drying condition, three sections of the samples were cut by a sledge microtome. As shown in Figure 5.1, the size of each sample was 10(R)×10(T)×10(L) mm. In total, 50 sapwood samples and 50 heartwood samples were used in this experiment.

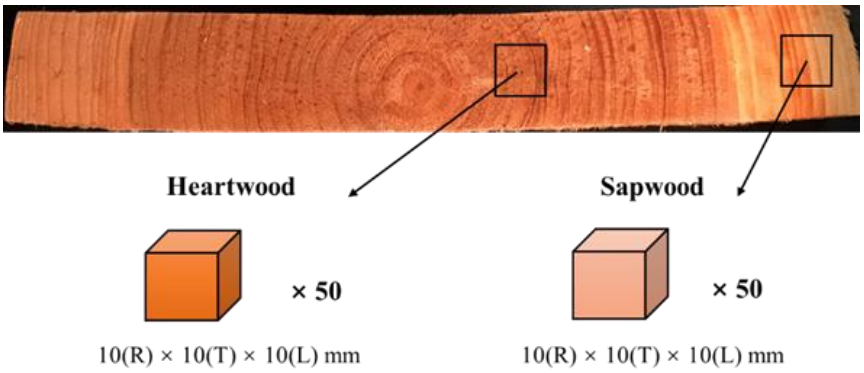


Figure 5.1 Sapwood and heartwood samples were cut from *C. lanceolata*.

5.3.2 Low-molecular Weight Phenolic (LMWP) Resin Penetration

Forty percent LMWP resin solution was supplied by Kyushu Mokuzai Kougyou Co., Ltd. (Uchikura 2009, Hermawan et al. 2013). A total of 50 *C. lanceolata* samples were impregnated. The impregnation process of the wood is shown in Figure 5.2. The resin solution was diluted to 10% concentration with 5°C distilled water. All of the samples in this experiment were placed in 60°C drying conditions for more than two days before impregnation. The samples were impregnated with five cycles of alternating barometric pressure and negative pressure. The impregnated samples were air-dried for one week. Then the samples were dried for three days at 60°C. Finally, the samples were heated at 130°C for two hours. After impregnation, the samples were cooled and the preparation process was completed.

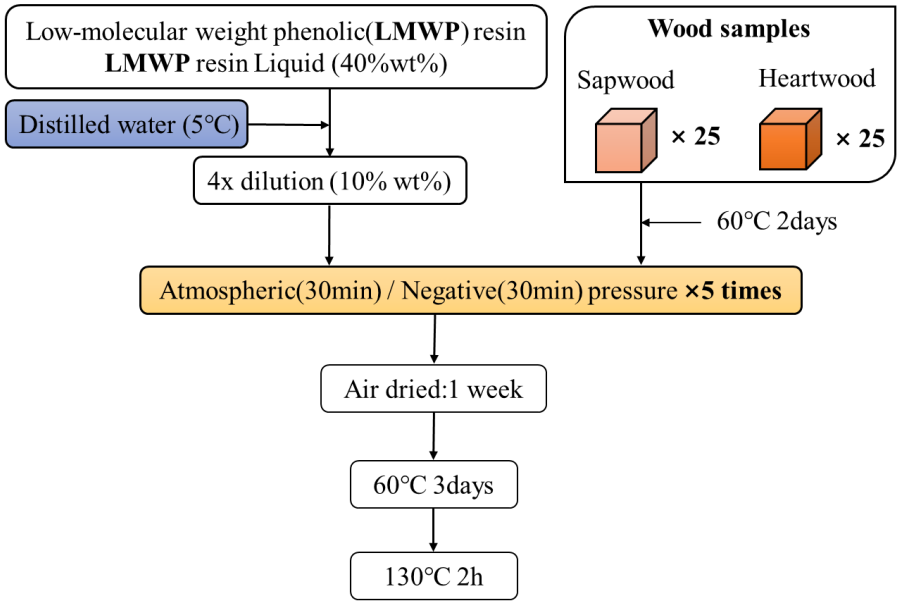


Figure 5.2 The preparation procedure of Low-molecular weight phenolic (LMWP) resin penetration.

5.3.3 Natural Weathering Conditions

In the summer of 2018, this experiment was conducted in Fukuoka (latitude 33°north), Japan, as shown in Table 5.1 (Japan Meteorological Agency 2018). All of the samples were placed outdoors for four weeks. According to JIS K 5600-7-6, all of the samples were placed in a south-facing position at a 45°angle from the horizontal. After seven days of exposure, all of the samples were removed from the weathering racks, measured in the laboratory, and then put back on the weathering racks to continue the exposure experiment. The experiments were repeated after 14 days, 21 days, and 28 days (Kataoka and Kiguchi 2009). After each exposure, it was necessary to gently remove the dust with nitrogen to ensure that the sample surface was clean.

Table 5.1 Weathering conditions in Fukuoka during summer 2018.

Weather Condition	Temperature (℃)	Humidity (%)	Sunshine Duration (h)	Rainfall (mm)	Wind Speed (m/s)
Mean Value ± SD	30.01±1.41℃	67.81±6.31	9.13±3.57	1.68	2.92±0.80

Note: the parameters show the average and standard deviation (SD) during July and August 2018 (N=62).

5.3.4 Color Measurements

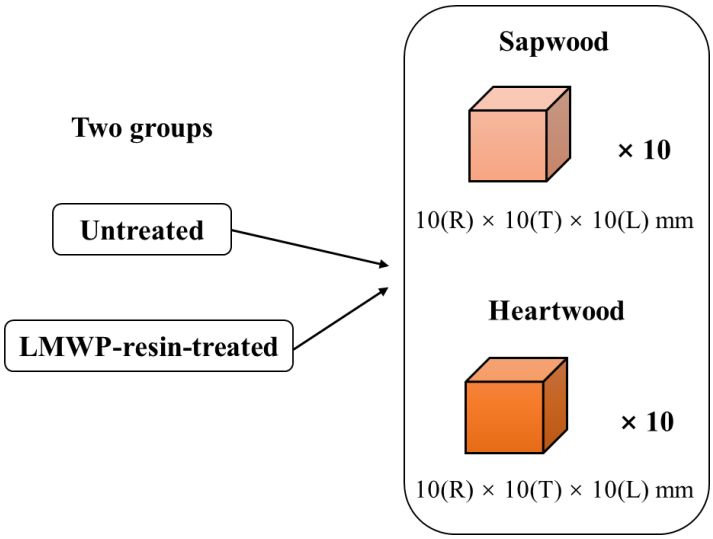


Figure 5.3 Samples for color analyses testing.

The CIE L* A * B * system was used to evaluate the color change of the sample surface after each exposure period (Kataoka and Kiguchi 2009). A colorimeter (Model NR-3000, Nippon Denshoku, Tokyo, Japan) was used as the test instrument in this experiment. Using the D65 standard illuminant and the 2°standard observer in the color measurement, the degree of color change L * (lightness), a * (redness), and b * (yellowness) were measured. As shown in Figure 5.3, there were 40 color measurement samples. Each sample chord tangent was measured 30 times. The average values and the standard deviation for each sample were calculated. Then the color changes were calculated according to the following formulas. △C* indicates chroma difference. △E* represents the total color difference. △H* is the difference in hue (Robertson 1977, Tolvaj and Faix 1995).

$$C^* = \sqrt{a^{*2} + b^{*2}} \tag{1}$$

$$\Delta C^* = C^* - C_o^* \tag{2}$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{3}$$

$$\Delta H^* = \sqrt{\Delta E^{*2} - \Delta L^{*2} - \Delta C^{*2}} \tag{4}$$

5.3.5 Low-Vacuum Scanning Electron Microscopy (LVSEM)

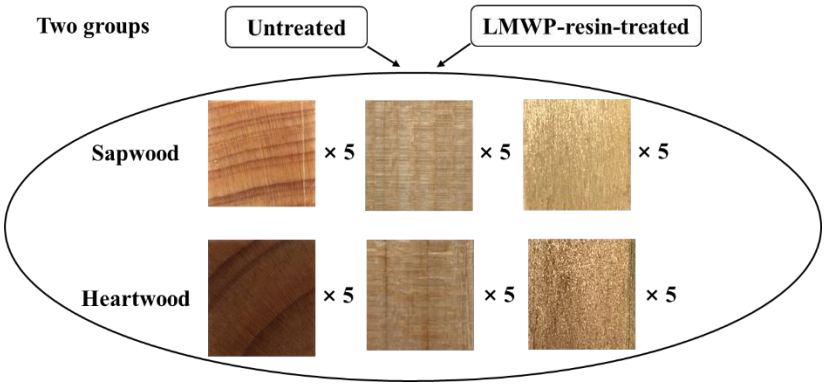


Figure 5.4 Microstructure observation samples.

In this experiment, 60 uncoated samples before and after exposure were observed with low-vacuum scanning electron microscopy (LV-SEM, Model JSM-5600LV, JEOL, Tokyo, Japan), as shown in Figure 5.4. The operating conditions of the microscope were as follows: a voltage of 15 kV, a pressure of 10–30 Pa, and a working distance of 10–20 mm. The LVSEM method was used to compare and observe the wood surface of the same part before and after exposure (Hatae et al. 2012a, 2012b).

5.4 Results and Discussion

5.4.1 Microstructure observation

These findings were in accordance with other studies that had shown that weathering caused rapid and extensive physical and chemical changes to wood surfaces (Miniutti 1964, Evans et al. 1996). However, unlike previous studies, we were able to non-destructively follow the time-dependent micro-structural changes for wood surfaces exposed to weathering (Hatae et al. 2012a, 2012b).

Untreated and LMWP resin treated wood

Figure 5.5a shows a backscattered electron image of the cross sections of untreated *C. lanceolata* sapwood before natural exposure. There were no checks or cracks in the tracheid walls in either the earlywood, latewood, or ray parenchyma. Figure 5.5b-e shows the backscattered electron images of untreated wood that was exposed to natural weathering for 7 days, 14 days, 21 days, and 28 days. The cell wall areas shown in Figure 5.5b-e were the same as those shown in Figure 5.5a. Every tracheid wall and compound middle lamella at the wood surface became thin and eroded as a result of exposure to natural weathering for 14 days (Figure 5.5c). Part of the earlywood tracheids at the growth ring boundary was also degraded and checked. Moreover, the check occurred between the tracheid and ray parenchyma. The thickness of the tracheid walls decreased and the erosion in the compound middle lamellae was enlarged following additional exposure for 28 days, which caused the separation of the earlywood and latewood at the growth ring boundary as previously suggested (Evans 1989). As shown in Figures 5.5k-o, the thinning of the tracheid walls and the erosion in the compound middle lamellae occurred easily with the *C. lanceolata* heartwood exposure to natural weathering. After 28 days (Figure 5.5o) of weathering, the tracheid walls became thinner and the compound middle lamellae became more eroded.

We compared the micro-structural changes in the LMWP-resin-treated wood

exposed to artificial weathering with similarly exposed untreated wood, as mentioned above. Figure 5.5f shows a backscattered electron image of the transverse surface of LMWP-resin-treated *C. lanceolata* sapwood before natural weathering. There was no thinning of the tracheid walls or erosion in the compound middle lamellae, as expected. Figures 5.5g-j shows the backscattered electron image of the LMWP-resin-treated sapwood exposed to natural weathering for 7 days, 14 days, 21 days, and 28 days. As shown in Figure 5.5h, the tracheid walls did not have checks in either the earlywood or latewood, and the compound middle lamellae were not eroded. No checks were evident in the ray parenchyma. Figure 5.5j shows an image of a LMWP-resin-treated wood surface exposed to natural weathering for 28 days. The tracheid walls became thinner and the compound middle lamellae slightly eroded after exposure for 28 days. Most of the tracheid walls had tiny checks in the latewood. Even the tracheid wall of the earlywood became thinner, although this was not enough to separate the earlywood and latewood at the growth ring boundary. In other words, the structural degradation occurred more slowly in the LMWP-resin-treated *C. lanceolata* than in the untreated wood.

Figure 5.7a shows a backscattered electron image of a radial section of untreated *C. lanceolata* sapwood before natural weathering. There were no checks and cracks in the cell walls of the tracheids or ray parenchyma. In addition, the bordered and half-bordered pits were not damaged by the surface preparation. Figures 5.7b-e shows the backscattered electron image of the untreated wood, which was exposed to natural weathering for 7 days, 14 days, 21 days, and 28 days. Every bordered and half-bordered pit at the wood surface was checked as a result of exposure to natural weathering for 7 days (Figure 5.7b). The direction of these checks appeared to follow the orientation of the microfibrils in the secondary wall. Some of the cell walls of the tracheids were also degraded (Figure 5.7c). Figure 5.7e shows an image of an untreated sample exposed to natural weathering for 28 days. The location of the cell wall surface in the image was the same as that in Figure 5.7a. The dimensions of the checks in both the bordered and half-bordered pits increased following 28 days of exposure to natural weathering.

Furthermore, some checks in the half-bordered pits in the ray parenchyma merged to form a larger check (Figure 5.7e). Some checks in the bordered pits in the tracheids also merged to form larger checks. This enlargement of pits checks caused the upper surface layer of the tracheids to exfoliate. As a result, the underlying tracheids were exposed to weathering, and new pit micro-checks developed. As shown in Figures 5.7k-o, extensive pit micro-checking developed in the *C. lanceolata* heartwood exposed to 0 days, 7 days, 14 days, 21 days, and 28 days of natural weathering. Individual checks became enlarged and merged together with increasing exposure, and the exfoliation of the upper-most layer of tracheids was apparent after only 7 days (Figure 5.7l) of weathering. After 28 days of weathering exposure, the surface microstructure was completely destroyed (Figure 5.7o). It would have been difficult to identify the original surface anatomical structure if we had continued the experimental observation.

Figure 5.7f shows a backscattered electron image of a radial surface of the LMWP-resin-treated *C. lanceolata* sapwood before natural weathering. There was no checking of the pits, as expected. Figures 5.7g-j show the backscattered electron images of the LMWP-resin-treated sapwood exposed to natural weathering for 7 days, 14 days, 21 days, and 28 days. The cell wall surfaces shown in Figures 5.7g-j were the same as those shown in Figure 5.7f. Pit checking was evident in some tracheids (Figure 5.7g). However, only a few micro-checks developed in the half-bordered pits in the ray parenchyma (Figure 5.7h). In addition, checks developed in the half-bordered pits in an axial parenchyma cell. However, some intact (unchecked) half-bordered pits in the rays were still present in the LMWP-resin-treated and weathered surface. Furthermore, checks in the treated wood surfaces exposed to natural weathering for 28 days were smaller than those of the checks in the untreated wood surfaces for the same period of time (Figure 5.7j). Figure 5.7p shows an image of an LMWP-resin-treated wood surface unexposed to natural weathering. As shown in Figure 5.7q-t, the locations of the cell wall surfaces in the images were the same as those shown in Fig 5.7p. After 28 days of exposure, the checks in the bordered and half-bordered pits in the LMWP-resin-treated samples, which were apparent after 14 days of exposure, had increased in size, but not

as much as the checks in the untreated samples exposed to natural weathering for 28 days (Figure 5.7o). The checks in both the bordered and half-bordered pits followed the orientation of the microfibril in the secondary walls, in accordance with the observations of checking in the untreated wood (Figure 5.7r, s, t). In other words, the structural degradation was less extensive in the LMWP-resin-treated wood than in the untreated wood.

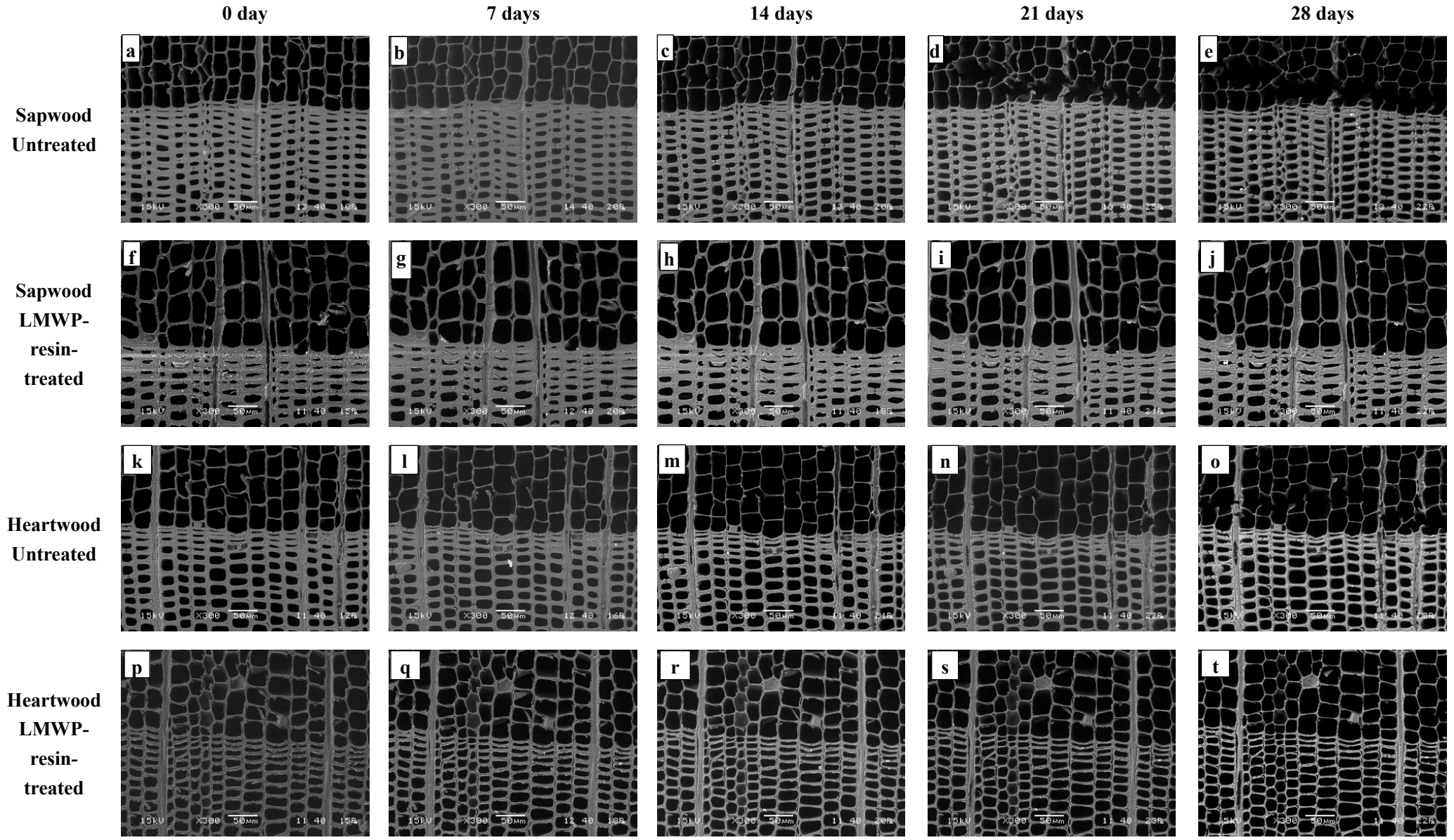


Figure 5.5 LVSEM of cross sections of untreated and LMWP resin treated wood before and after natural exposure.

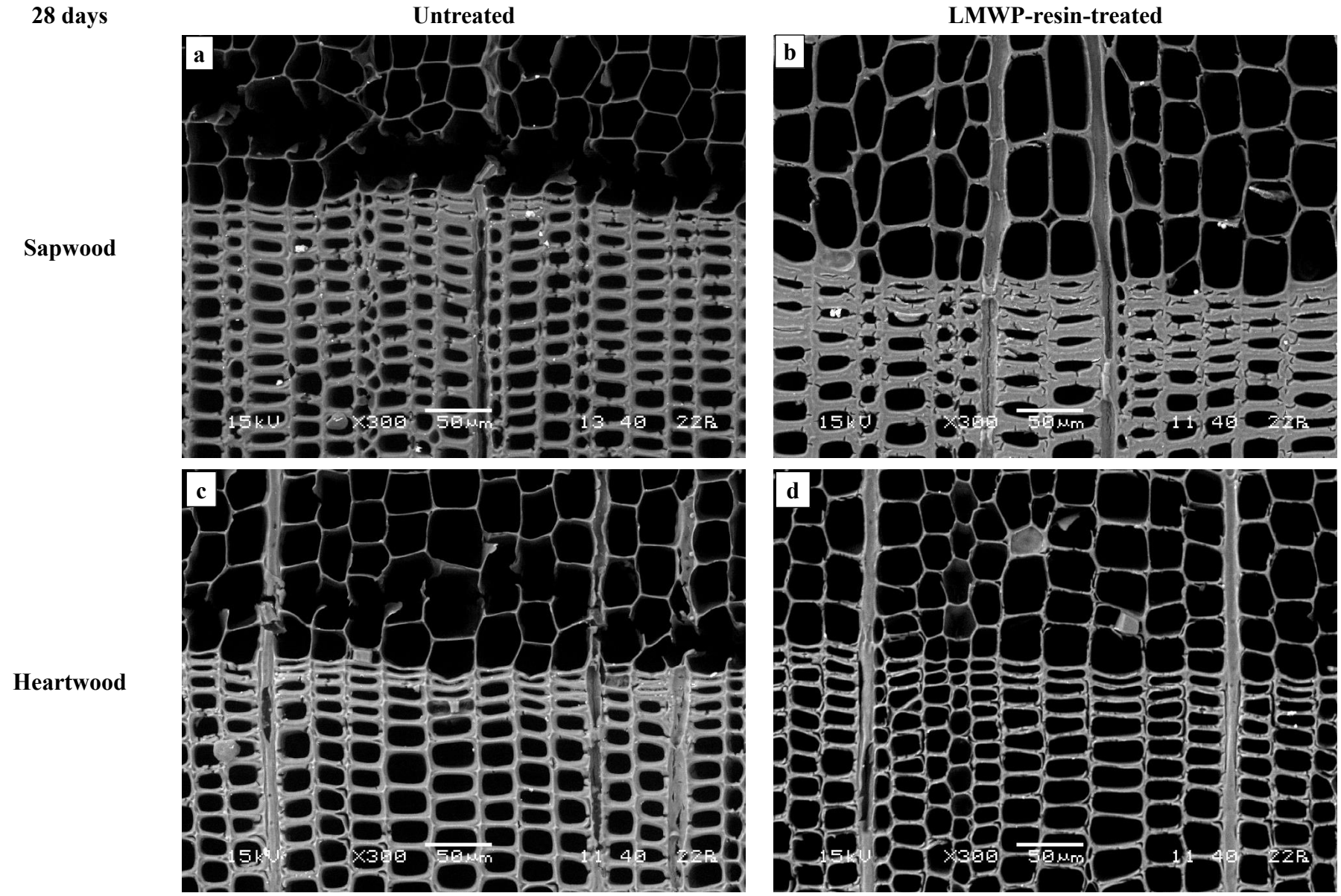


Figure 5.6 LVSEM of cross sections of untreated and LMWP resin treated wood between sapwood and heartwood after natural exposure 28 days.

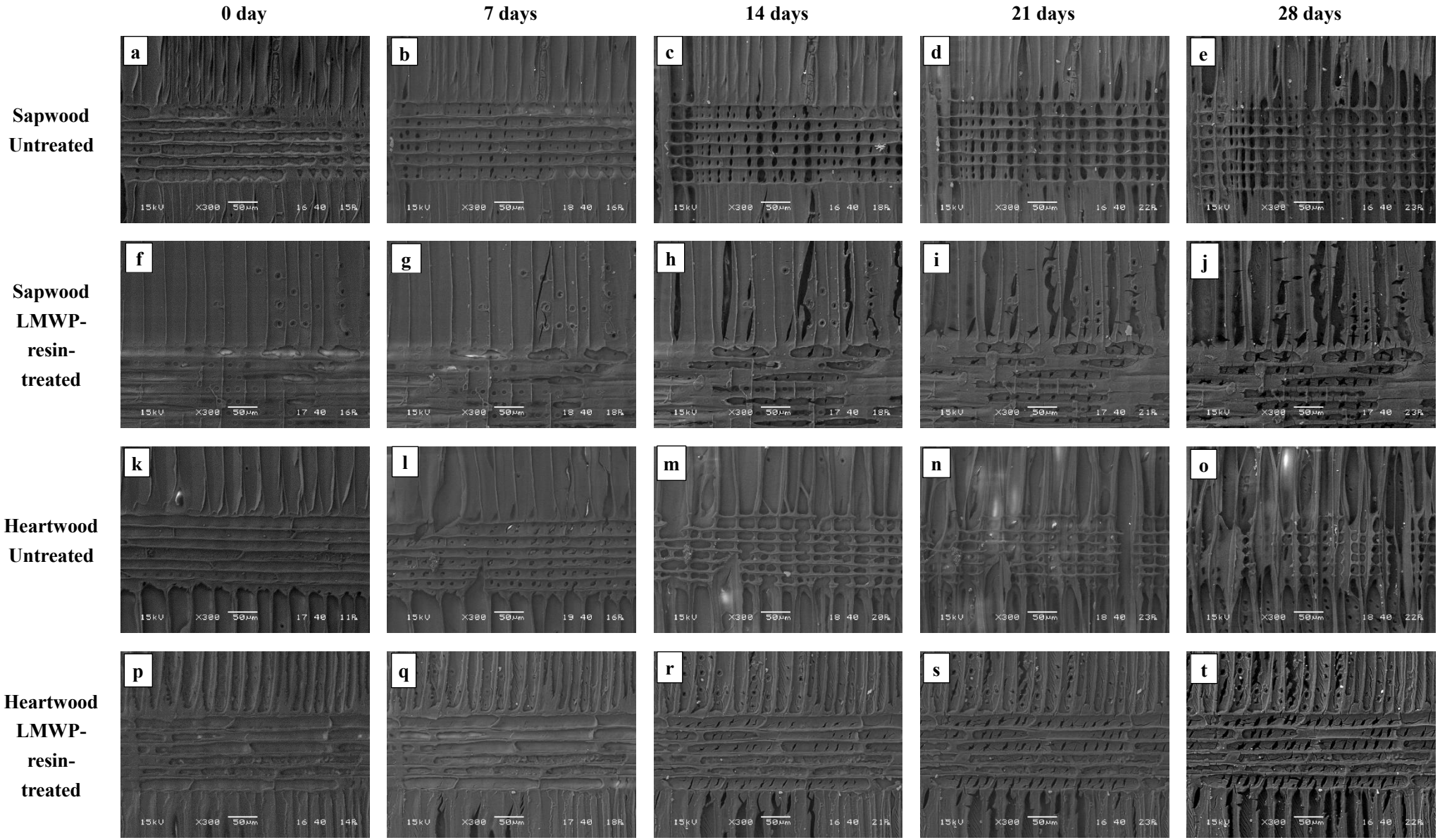


Figure 5.7 LVSEM of radial sections of untreated and LMWP resin treated wood before and after natural exposure.

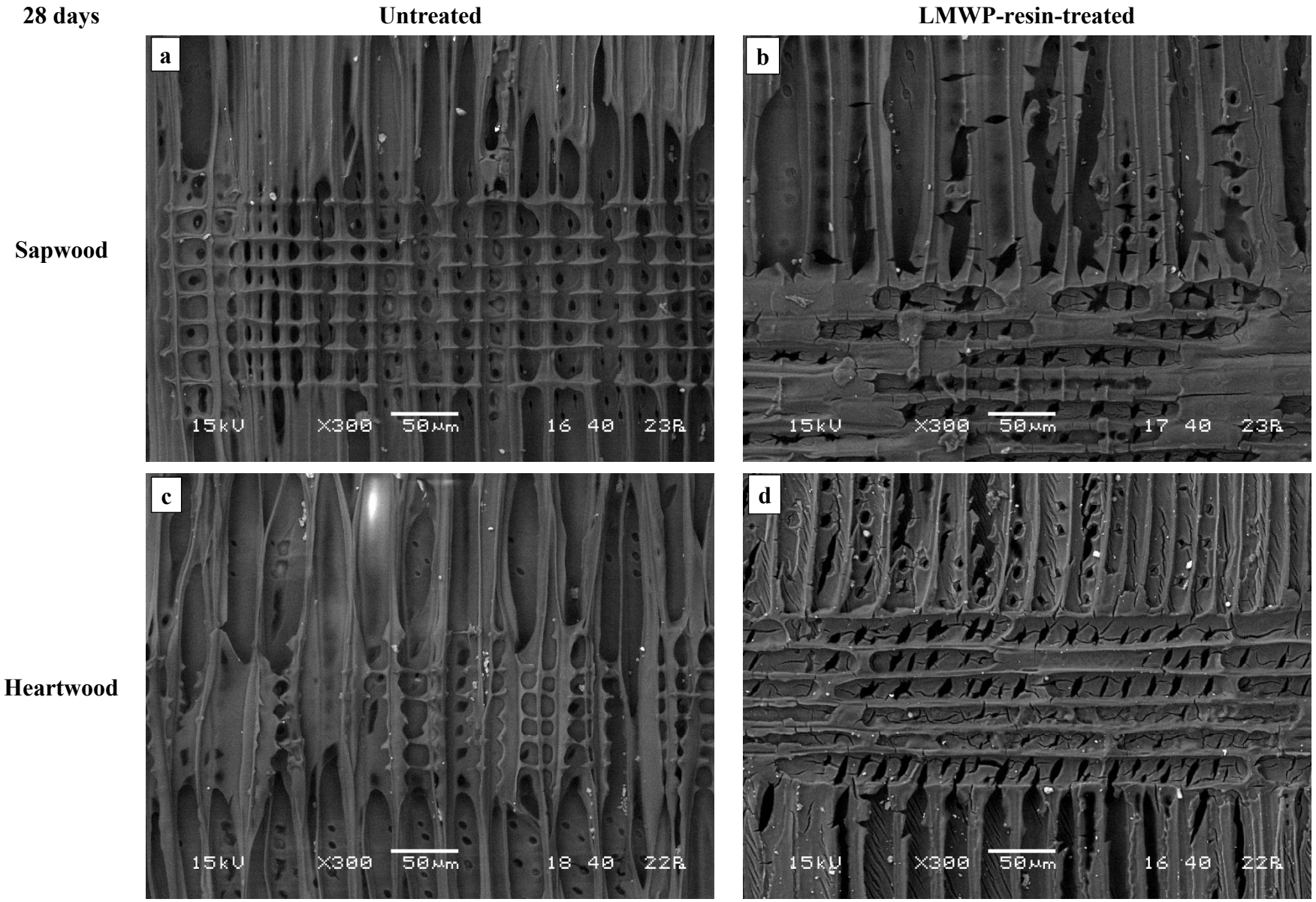


Figure 5.8 LVSEM of radial sections of untreated and LMWP resin treated wood between sapwood and heartwood after natural exposure 28 days.

Sapwood and heartwood

Figure 5.6 shows the cross sections of the *C. lanceolata* sapwood and heartwood after 28 days of natural weathering. Compared with the heartwood and sapwood treated with LMWP resin, it was found that the weathering resistance of the sapwood was better than that of the heartwood. Although the cell wall of the *C. lanceolata* treated with LMWP resin was cracked, the cell wall structure was intact, and the cell wall became thinner. Figure 5.8 shows the radial sections of the *C. lanceolata* sapwood and heartwood after 28 days of weathering. After comparing the position of pits, tracheids, and cross fields, it was found that the LMWP-resin-treated sapwood structure was more complete than the same treated heartwood structure. At that time, the surface microstructures (especially those of the heartwood) of the untreated groups were completely destroyed. The results showed that the method of LMWP resin impregnation had a significant effect on improving the weatherability of the *C. lanceolata*.

5.4.2 Discoloration of Wood Surface

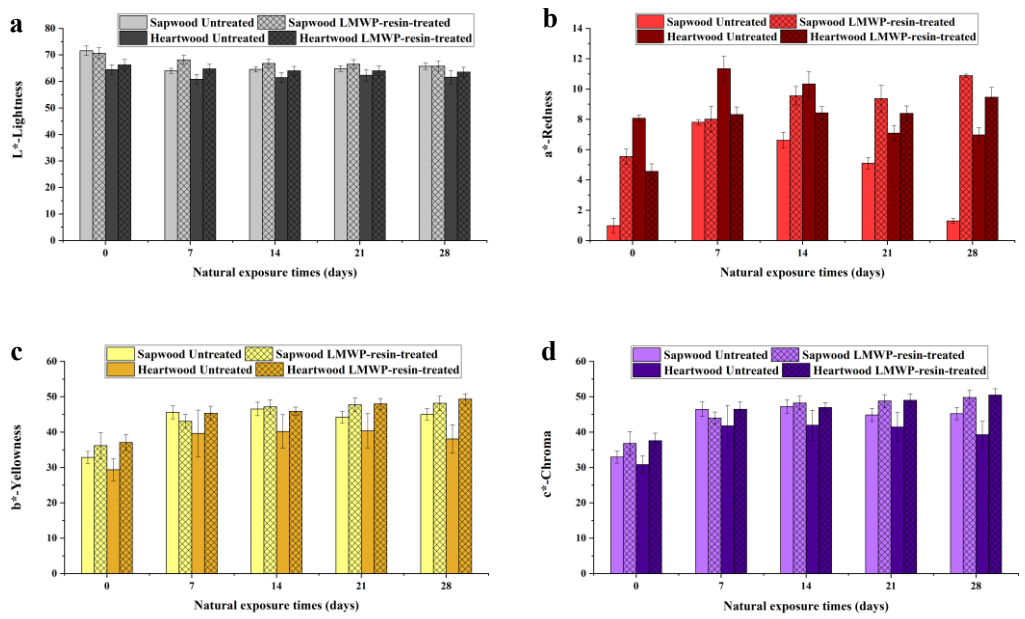


Figure 5.9 Color modifications of the samples: (a) Lightness L*; (b) redness a*; (c) yellowness b*; (d) chroma c*.

The color changes of all samples within four weeks of exposure are shown in Figure 5.9. The effects of natural exposure on △E*, △C*, and △H* are shown in Figure 5.10. The values of △E* (total color difference), △C*(color difference), and △H*(color difference) for the untreated and LMWP-resin-treated wood increased rapidly in the initial seven days. The △E* values for the LMWP-resin-treated groups were lower than those for the untreated groups, and the sapwood resin-treated groups had the lowest gain. After two weeks, the total color difference of the untreated groups began to decline. However, this phenomenon was not found in the LMWP-resin-treated wood. This indicated that the untreated and resin-treated samples exhibited different discoloration reactions during four weeks of natural weathering.

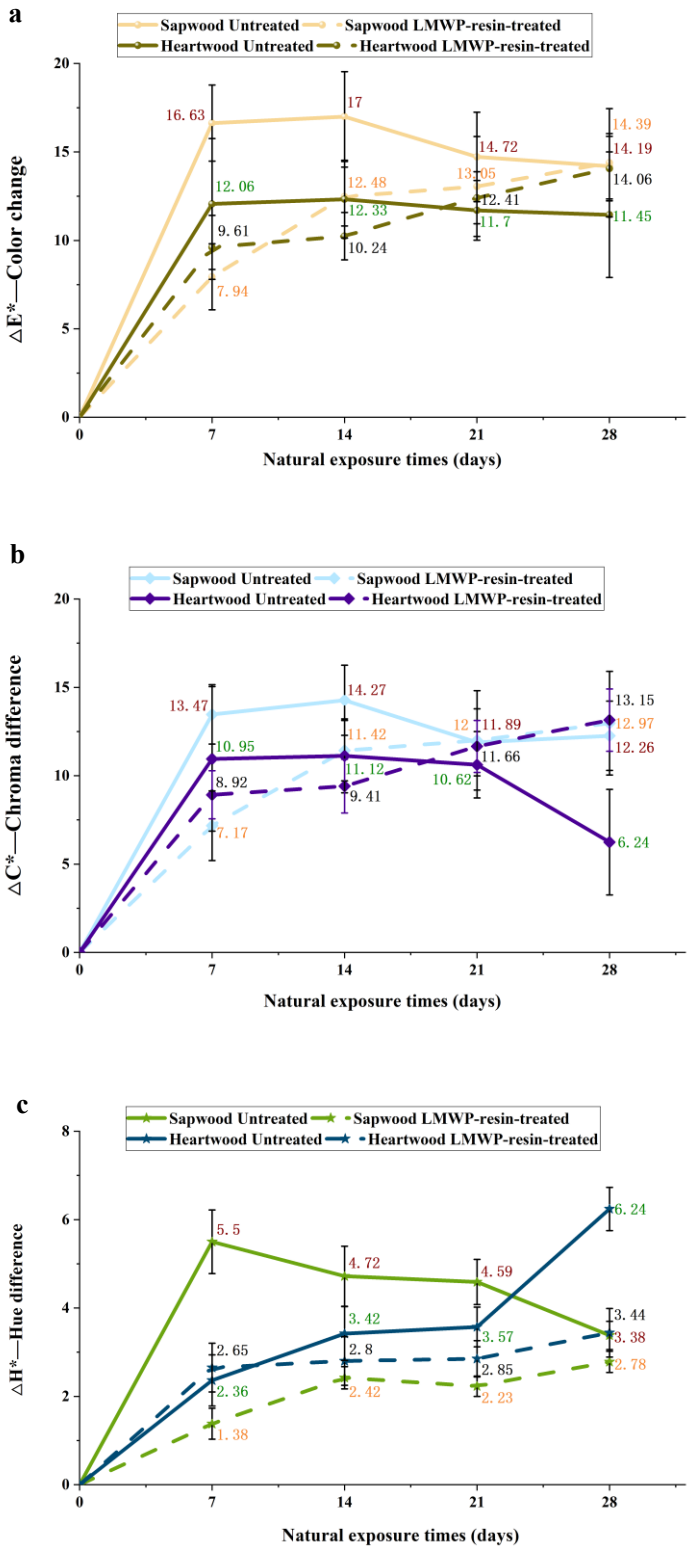


Figure 5.10 Color changes of wood samples: (a) Chroma difference △C*; (b) color change △E*; (c) hue difference △H*.

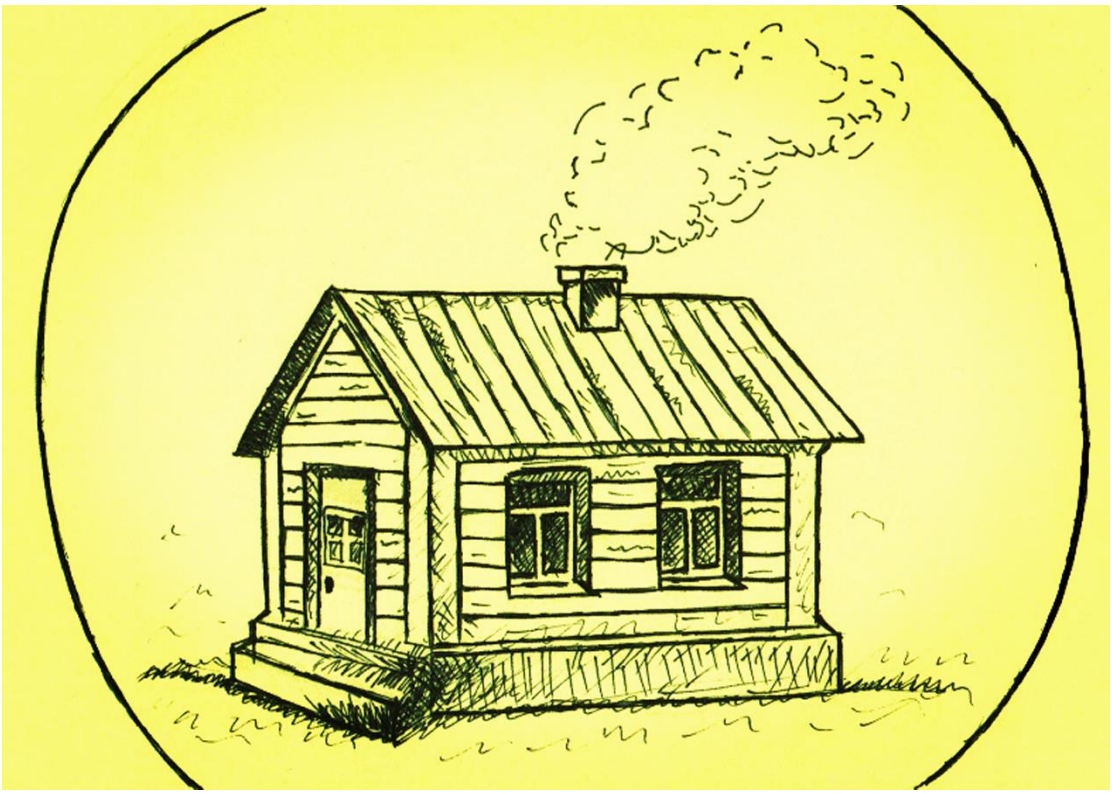
In this study, there were two potentially favorable color stability reasons for the wood resin treatment with natural weathering. First, the resin treatment was not sufficient to significantly change the chemical composition of the wood. Second, the resin treatment strengthened the wood structure, isolated part of the light radiation, and inhibited the color change. After the resin treatment, the color change of the wood after natural exposure was weakened and the color stability was improved. For the resin-treated heartwood, it was inferred that due to the influence of extracts, the color stability in the early stage was not as significant as that of the sapwood after resin treatment.

In summary, it could be seen that in the natural weathering process, resin treatment could improve the structural stability of the wood and play a certain color stability role in the early stage of weathering. These advantages played a positive role in the natural weathering of the wood. In particular, the degradation resistance of the wood was greatly improved and the negative effect caused by natural weathering was alleviated. However, the different effects of resin treatment on sapwood and heartwood of the same species might be affected by some of the wood chemical components. In the process of resin treatment, detailed chemical analysis should also be carried out, which will be the focus of future research.

5.5 Conclusions

The natural weathering experiment lasted for four weeks, during which time changes in the color and the surface structure were periodically assessed. We used untreated wood for comparison. The LVSEM revealed that the impregnated wood degraded more slowly when weathered than the untreated wood did. After four weeks of weathering, the microstructure of the radial sections of the untreated wood was basically damaged. The impregnation treated maintained color stability during the initial weathering. In this way, this process weakened the color change. The results confirmed that the durability of the *C. lanceolata* was improved by impregnation with low molecular weight phenolic resin. This study may play a positive role in the long-term stable utilization of *C. lanceolata* and the extension of the service life of wood products.

CHAPTER 6 General Discussion, Conclusions and Recommendations



6.1 General discussion

To study the weathering resistance of wood, the weathering protection method of wood was established and perfected under this research. Different physical or chemical methods were used to treat wood weatherability based on different causes of wood weathering. Treating wood effectively is an important way of improving its weathering resistance and extending the service life of wood products. Accordingly, the cost of maintaining wood structures is reduced (Feist 1989). Many studies have been carried out to improve the weatherability of wood.

The overall objective of this study was to improve the weathering resistance of *C. lanceolata* and to provide clear information on basic weathering behavior and the effects of heat treatment and low-molecular-weight phenolic resin impregnation on the weathering resistance of this species. The results can provide relevant information for the degradation characteristics of *C. lanceolata* before and after treatment in natural environments and provide a basis for establishing and perfecting the weathering resistance pretreatment strategies for this species. The results also provide a basis for improving the effective utilization of *C. lanceolata*.

In Chapter 3, the variation of internal weathering behavior of *C. lanceolata* was discussed. Through outdoor short-term exposure experiments, the differences in growth in the radial and axial directions were observed for this species. The color change on the surface of the wood was obvious from the beginning. No structural changes were detected until a week after exposure. However, the surface microstructure of *C. lanceolata* was severely damaged after one month of exposure. The color change of the wood surface was inhibited by the extract at the early stage of exposure. During natural weathering, the structures of the middle lamella and primary cell walls were destroyed quickly. Consistent with the conclusions of many previous works, lignin has been reported to be the most sensitive chemical component in wood photodegradation (Evans et al. 1996, Pandey 2005, William and David 1984). By observing the

degeneration of the cell wall in the cross section after a month of natural weathering, we found that only the skeletal structure was left. When lignin absorbed ultraviolet light on or near the surface of the wood, lignin degraded the most profoundly, followed by hemicellulose and cellulose. Cellulose is more resistant to photodegradation than hemicellulose due to its high molecular weight and the protection of its crystal structure (Kollmann et al. 1975, Shmulsky and Jones 2019, Nicholas 1982). In the present study, the condition of the anatomical structure of the heartwood and sapwood in *C. lanceolata* before and after weathering was compared. The results showed that weathering had different effects on heartwood and sapwood. During weathering, the surface structure of *C. lanceolata* differed at different heights. After a week of weathering, the surface structure of *C. lanceolata* began to degenerate, especially at 4 m. One month later, the surface of the wood was severely damaged. The comparison showed that the damage at a height of 1 m was the least pronounced and that at a height of 4 m was slightly heavier. The structure of the surface of the wood varied slightly along the axial height. It was inferred that the weathering resistance of *C. lanceolata* substrate was stronger than that of top timber. The weathering behavior of *C. lanceolata* was also positively correlated with wood density; where the density was high, the weathering resistance was strong, and vice versa. The weathering resistance of *C. lanceolata* was related to the characteristics of the species; thus, improving the basic properties of the wood, such as density, would have a positive effect on the weathering resistance of the wood.

In chapter 4, heat-treated and untreated *C. lanceolata* samples were exposed to natural conditions for one month. The physical and anatomical changes of the surface of the wood were detected using different analytical methods. Anatomical sites with high lignin content showed more serious deterioration during natural weathering. At higher treatment temperatures, the relative content of lignin depended more on the degradation of hemicellulose (Funaoka et al. 1990, Cheng et al. 2016). Under natural exposure conditions, the decay of the anatomical sites with high lignin content was more pronounced. We concluded that heat treatment did not improve the structural stability of wood. Rather, it exacerbated the decline in the integrity of the anatomical

structure. Both 190°C and 220°C heat treatments accelerated the aging phenomenon, and these results differed only in degree. These trends contradicted the results of color stability. The heat-treated wood can improve the dimensional stability of the wood, maintain uniform wood color, and most importantly prevent degradation caused by microorganisms and insects (Alfred et al. 1946, Esteve and Pereira 2009, Kocaefe et al. 2008). These advantages have a very positive effect on the natural strength of wood. In particular, there is less damage induced by microorganisms and insects, greater resistance to degradation, and a less pronounced effect of decay induced by natural weathering. However, because heat treatment reduces the mechanical strength and structural stability of wood, heat treatment as a means of rainproofing wood should be evaluated comprehensively. During heat treatment, the change in mechanical strength and structural stability should be considered. We plan to study this in a future work. The advantages of heat treatment technology are that it can improve corrosion resistance, limit the loss of mechanical strength and structural stability, and support weathering resistance of wood, and so improve the overall utilization of wood.

In chapter 5, the use of low-molecular-weight phenolic resin in the prevention of surface weathering on *C. lanceolata* wood is discussed. The durability of *C. lanceolata* is relatively low. The weatherability of *C. lanceolata* could be improved by impregnating the wood with low-molecular-weight phenolic resin. The natural weathering experiment lasted for 4 weeks, during which time, changes in color and surface structure were periodically assessed. The changes in microstructure were studied by LVSEM. The results showed that the impregnated wood degraded more slowly when weathered than did untreated wood. The impregnation treated maintained color stability during weathering. It could also prevent the leaching of depolymerized lignin and wood extracts. In this way, this process weakened the color change. *C. lanceolata* impregnated with low-molecular-weight phenolic resin showed good weathering resistance after 4 weeks of weathering. We used untreated wood as a reference. After 4 weeks of weathering, the microstructure of the radial sections of the untreated wood had been basically damaged. The results confirmed that the durability

of *C. lanceolata* was improved by impregnation with low-molecular-weight phenolic resin. This study may play a positive role in the long-term stable utilization of *C. lanceolata* and extension of the service life of wood products.

It is obvious from the changes in the wood market in recent years that the use of traditional wood treatment methods is becoming increasingly limited due to environmental problems. Chemically and thermally modified wood may be a valuable alternative to traditional preservation methods and may become important in various applications. Modifying the chemical composition of the wood increased its weathering resistance. These modification treatments have become alternatives to traditional wood protection. Among the various chemical modification methods known at present, only a few have been developed on the industrial scale. Improving durability depends on the nature of the modification method used. Heat treatment products have been successfully commercialized in several European countries. Some researchers have explored modifications of chemical impregnation (Gérardin 2016).

6.2 Conclusion

First, the weathering behavior of *C. lanceolata* was studied. The changes in the color of the wood surface were readily visible from the beginning. Observed structural changes were not detected until a week after exposure. However, after one month of exposure, the surface microstructure of *C. lanceolata* was severely damaged. The change in the color of the wood surface was inhibited by the extract at the beginning of exposure. However, the weathering resistance of heartwood was still found to be lower than that of sapwood as exposure continued. The weathering behavior of *C. lanceolata* increased in the axial direction from bottom to top. The photodegradation rate of the wood decreased with the increase of density. Second, the change in the color of the surface of *C. lanceolata* after 190°C heat treatment was inhibited to a profound extent in the natural weathering process. Heat treatment played a positive role in maintaining the physical properties of the wood. LVSEM studies showed that heat treatment aggravated the degradation of the wood structure of *C. lanceolata* under natural

conditions. Thermal modification is not conducive to the maintenance of structural stability. When heat treatment is used as an anti-weathering treatment method, practitioners should consider both the advantages and disadvantages of thermally modified wood. Finally, impregnation resin treatment was used to prevent weathering. Low-molecular-weight phenolic resin was found to attach to cell wall infusion, and the cell walls were reinforced. The changes in the surface of the treated wood decreased during natural weathering conditions. The selection of weathering treatment to improve wood durability must meet the two basic goals of safety and effectiveness. In conclusion, this study provides a reference for weatherability research of *C. lanceolata* under natural conditions. These results will make an important contribution to the sustainable utilization of *C. lanceolata*.

6.3 Recommendations

Wood industry experts should use the information obtained from this study on weathering behavior and sustainable use of *C. lanceolata* during weathering.

Weathering behavior is the basis of weatherability research. Modification is the prospect of wood weathering. In this study, the feasibility of heat treatment and chemical modification of *C. lanceolata* was obtained.

The results of this study are of great significance to continue to explore the weatherability plan of *C. lanceolata* to prolong the wood life cycle. Therefore, researchers of sustainable wood use should use the information obtained in this study to develop and improve weathering prevention schemes for the species.

The wood treatment methods used in this study are limited (only heat treatment and one impregnation treatment were discussed), and further research may be needed to refine the current study results. The disadvantages of heat treatment and the application of impregnation treatment in longer weathering time need to be further explored.

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