PHOTODEGRADATION OF ADHESIVES USED IN WOOD COMPOSITE MATERIALS

by

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Abstract

The weathering of wood composites is caused by a complex combination of chemical and mechanical effects. Wood composites such as glulam beams are increasingly being used outdoors where their service life depends to some extent on the durability of the adhesive used in the composite. Increases in the durability of adhesives used in such composite materials would prolong their service life and enable them to compete more effectively with other structural materials such as concrete and steel. This study attempted to improve our understanding of the photodegradation of adhesives and the relationship between wood and adhesive photodegradation. The effectiveness of a UV light absorber and hindered amine light stabilizer (UVA and HALS) at protecting adhesives from photodegradation was also investigated. First, the effect of adhesive type (melamine formaldehyde, epoxide, and emulsion polymer isocyanate), stabilizer and adhesive stabilizer interaction on tensile strength, weight loss and discoloration of adhesive dog-bone samples exposed in two different weatherometer devices (QUV and Xenon-arc) was examined. Structural and chemical changes of the adhesive specimens were examined using Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). Secondly, the effects of adhesive type (melamine formaldehyde, epoxide), stabilizer and adhesive stabilizer interaction on surface roughness and discoloration of wood-adhesive-dowel samples exposed to solar radiation was examined. Profileometry and SEM was used to examine the surface of dowels in the region where they were exposed to both wood and sunlight. An epoxide adhesive (butyl glycidyl ether of bisphenol-A with polyamide) used in the aircraft industry showed outstanding resistance to weathering. The other adhesives were not as resistance to weathering, but the addition of a UVA/HALS photostabilizer to the adhesives generally increased their photostability (particularly color changes of the epoxy adhesives and weight loss of the MF adhesive). Greater degradation of adhesive samples occurred when they were exposed in a QUV weatherometer than in a Xenon-arc weatherometer. The synergistic effect of moisture and UV radiation on the degradation of adhesives may account for this observation. Adhesive dowels embedded in wood did not show greater degradation (erosion) in the region where they were exposed to both wood and sunlight. Therefore the hypotheses that wood photosensitizes adhesives could not be supported by experimental findings. Further refinement of the experimental methodology developed in this thesis would be desirable to retest this hypothesis. All of the four adhesives that were tested possessed some interesting characteristics that might make them suitable for use in glulam exposed outdoors, but out of the four the two epoxy adhesives appeared to have the greatest potential.

Table of Contents

List of Tables

List of Figures

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1. General Introduction

According to Amstock (2001) the term glue refers to a sticky material, whereas adhesives don't have to be sticky. Adhesive is more inclusive, but in the past these two terms have been considered synonymous (Amstock 2001). For example, organic adhesives, coatings or cellulose are based on polymers and their organic chemistry shares some similarities (Stevens 1999). Therefore, they are sometimes treated as equivalent in this work.

As Keimel (1994) mentioned, the history of adhesives is closely related to the history of humankind. The first commercial glue plant was founded in 1690 in Holland. At that time the majority of glue applications were for the manufacturer of furniture (Amstock 2001). Today the fields of applications for adhesives are manifold and they surround us in nature and in our daily lives. Applications abound from office "post-it notes" to automotive safety glass to footwear to aerospace structures to "no-lick" postage stamps to bonding wood. Many products that we take for granted could never exist if it were not for adhesive bonding (Petrie 2007). According to market research conducted by Freedonia, the World market value for adhesives was estimated approximately to 25 billion U.S. dollars in 2004 (Phänomen Farbe 2001). The largest regional markets are North America, Western Europe, and the Far East. These regions account for 85 % of the global demand by volume and 78 % of the value of adhesives (Petrie 2007). Furthermore, the world market for adhesives (and sealants) is growing by 3 % annually (Petrie 2007).

Major advancements in adhesive technology were made in the twentieth century (Amstock 2001). The development of modern and structural adhesives was closely tied to the development of aircraft and aerospace industries (Keimel 1994, Dowling 1945). High performance adhesives are particularly useful for this industry, because they save weight and are better in distributing stresses than mechanical attachment techniques such as bolting and riveting (Schultz and Nardin 1994). Another large-scale application of adhesives is in the construction industry for materials such as engineered wooden panels or glue laminated beams (glulam) (Amstock 2001, Phänomen Farbe 1999).

Glued laminated wood construction had its beginning at the turn to the twentieth century as a result of the activities of Otto Karl Hetzer in 1909, who obtained his first patent for glulam construction (Rhude 1996). Today large dimension engineered wood

composites, such as glulam beams, act as substitutes for steel and concrete for the construction of industrial and agricultural buildings and bridges (Mueller 2000). Petersen and Solberg (2002) reported that the manufacture and use of these materials consumes far less energy and thus generates lower levels of carbon dioxide than comparable steel products. Glulam also looks nicer than steel beams and it can be used to create distinctive buildings that people enjoy working in (Mueller 2000). Steel and concrete, however, are less susceptible to decay, fire and weathering than engineered wood composites.

A topic that is comprehensively discussed in the literature, which is of relevance to the performance of glulam exposed outdoors, is the complex effect of environmental factors (water, oxygen, heat and radiation) on adhesives and polymers. Such a topic is important because of the negative impact of environmental factors on the long term durability of adhesive bonds (Cotter 1977, Comyn 1998, Kerr, MacDonald, and Orman 1970, Althof 1981, Jellinek 1983, Kockott 1988, Dorn and Breuel 1992, White and Turnbull 1992, Stevens 1999, Akmal and Usmani 2000, Searle 2000, Keene et al. 2001). Also the price dependency of synthetic adhesives on their raw-material petroleum (Phänomen Farbe 2001); calls for a better understanding of the degradation mechanism of adhesives, leading to improvements in the protection of adhesives of adhesives and longer service lives for composites.

UV light is the driving force behind the degradation that occurs when polymers are exposed to the elements (Keene et al. 2001 and Searle 2000). According to Torikai (2000), polymeric materials contain functional groups (chromophores), which are capable of absorbing UV light and leading to chemical changes in the parent polymer. The two critical modes of photodamage applicable to most natural and synthetic materials exposed to solar radiation are yellowing discoloration and loss in mechanical integrity (Andrady et al., n.d.). More solar radiation and solar radiation of shorter-wavelengths now reaches the earth surface, as a result of partial ozone depletion in the atmosphere, which further decreases the lifetimes of polymeric materials such as adhesives (Torikai 2000). Different approaches have been taken to protect adhesives against UV radiation. Light stabilizers may be incorporated into the adhesive matrix in order to protect it against photo-induced degradation (Horsey 1994). Other additives such as antioxidants are also used to protect adhesives from oxidation (Horsey 1994, Comyn 1998). The patent literature on additives such as stabilizers and antioxidants is

2

voluminous (Rabek 1987). Glulam beams exposed outdoors may be coated with pigmented finishes, which provides some protection from photooxidative degradation, but such a coating also destroys the visual appeal of the glulam. The "Expo Dach" built for the World exhibition 2000 in Hannover/Germany (Figure 1.1), is constructed mostly from glulam (Bogusch and Seidel 2000).

Figure 1.1 has been removed due to copyright restrictions

Figure 1.1: The Expo Dach built for the World exhibition 2000 in Hannover/Germany (Janberg, n.d.)

The designers of this structure recognized the need to protect the glulam in the roof from weathering and to do this they stretched a thin translucent plastic over it (Burger 2000). This covering, which can be seen in the small picture in Figure 1.1, has helped to improve the service life of the glulam. In many situations, however, it is not possible to protect glulam by design and construction, and there may be a need to directly enhance the composite by increasing the photostability of the wood and adhesive.

However, there has not been much research on the photostability of adhesives used in glulam. Furthermore, as pointed out by Jordan (1989) it is important to examine not only the adhesive, but also the composite as a whole including adhesive and substrate (wood). In addition, it is mentioned in the literature, that individual observations of each material combination in a composite exposed to specific conditions is required, in order to evaluate its performance under these conditions (Dorn

and Breuel 1992). Therefore, this study was designed to examine the performance of selected adhesives under different artificial weather conditions and also to evaluate the interaction between wood and adhesive photodegradation, as it occurs e.g. in glulam beams exposed outdoors.

This study aimed to investigate the performance of adhesives exposed to artificial weather conditions including ultraviolet light. The ability of selective additives to stabilize adhesives and the influence of the wood matrix on adhesive photodegradation were also examined. Following this introduction, Chapter 2 reviews relevant literature on the effect of weathering factors (water, oxygen, radiation, pollution) on polymeric materials such as wood, adhesive and wood-adhesive composites and ways of stabilizing them. Experimentation in Chapter 3 examined the photostability of four different adhesives that could be used in glulam exposed outdoors. This research also examined whether a photo-stabilizer could protect the adhesive from photodegradation. The aim was to determine which adhesive type was most resistant to photodegradation and how effective the selected stabilizer mixture was at restricting photodegradation.

It is well known that metal compounds can accelerate the photooxidative degradation of polymers such as polyethylene and polypropylene (Shlyapnikov, Kiryushkin, and Martin 1996). Previous studies have found that the photodegradation of such polymers when used in wood plastic composites is accelerated by the presence of wood (Matuana, Kamdem, and Zhang 2001, Kiguchi et al. 2006). Therefore, it is reasonable to hypothese that the photodegradation of adhesives in glulam could be catalyzed by wood. Therefore, Chapter 4 examined the effect of solar radiation on the photostability of adhesive in contact with wood. A better understanding of the photostability of adhesives used in glulam and the factors that influence their photodegradation could help to prolong the service life of glulam exposed outdoors. More importantly, an extended service life for such products will help wood to become more cost effective and compete better with structural materials such as concrete and steel that cannot be produced sustainably.

2. Literature Review

2.1. Introduction

Adhesives are widely used today for a variety of different purposes. Wood composites such as glulam beams or wood plastic composites for example combine wood and adhesives (polymer) in one composite material. Organic materials, including most adhesive types and wood, however, are prone to degradation processes especially under outdoor conditions, and thus the lifetime of such materials is limited. Degradation caused by the environment comprises different factors; so the collective term weathering is used to describe it. Photodegradation refers to the degradation of a material caused by photons from highly energetic UV light. Better knowledge of the degradation of polymers, especially in composite materials, is not only of academic interest, but it is also of great practical importance. Rabek (1987) suggested that such knowledge could be used to improve stabilization through the development of more stable polymer structures, or by the introduction of more effective stabilizers. Alternatively, it could be used to help develop more "environmentally friendly" polymers which are designed to rapidly disintegrate outdoors when exposed to daylight, but are able to maintain their desirable mechanical properties during use under indoor illumination (Akmal and Usmani 2000).

2.2. Adhesives/Polymers - Adhesion

According to Schultz and Nardin (1994) the construction industry is the main field of application of adhesive bonding. The role of an adhesive is to bond two pieces in a fixed position. To achieve this goal the molecular attraction between the substrate and the adhesive (adhesion forces) and the molecular attraction by the adhesive throughout its mass (cohesion forces) have to be balanced (Sellers 1994). Adhesives have replaced in part the more classical mechanical bonding techniques of bolting or riveting. Adhesives are competitive primarily because they allow users to save weight, provide better stress distribution, and they offer better aesthetics since the glue-line can be practically invisible. Schultz and Nardin (1994) mentioned that adhesion became a serious area in scientific circles only about 50 years ago.

To perform satisfactorily, adhesives must be capable of both, wetting and penetrating the wood substrate and being converted into a rigid solid through either evaporation of the solvent, physical cooling in the case of a thermoplastic-type adhesive, or a chemical reaction that may require a catalyst and/or heat. Furthermore, the adhesives also need to polymerize to produce a stiff solid with adequate mechanical properties. As adhesives increase to a molecular weight of 500 g/mol or above useful cohesive strength is developed (Sellers 1994).

Schultz and Nardin (1994) pointed out that one of the main difficulties in the study of adhesion mechanisms lies in the fact that the subject is at the boundary of several scientific fields. This diversity is apparent in the number of theoretical models of adhesion that have been proposed (Schultz and Nardin 1994). The mechanism by which materials adhere together was classified by Filbey and Wightman (1988) into four categories: 1, electrostatic; 2, diffusion; 3, mechanical interlocking; and 4, adsorption. There are some discrepancies in the literature, however, regarding the classification of adhesion mechanisms. Petrie (2007) suggested that there are several theories attempting to describe adhesion. To the most common theories (mentioned above) he added the weak-boundary-layer theory, which is not described here.

Electrostatic adhesion results from the redistribution of charges that occurs when dissimilar materials are brought close together (Filbey and Wightman 1988). The electrostatic theory was proposed by Deryaguin and co-workers in 1948 and they suggested that electrostatic forces can have a significant contribution to adhesive strength (Schultz and Nardin 1994).

The diffusion theory states that polymer/polymer adhesion occurs due to interdiffusion of the macromolecular chains at the interface (Filbey and Wightman 1988). This theory, which was proposed by Voyutskii (1963), implies that the macromolecular chain or chain segments are sufficiently mobile and mutually soluble. The joint strengths mainly depend on factors such as contact time, temperature, nature and molecular weight of polymers, and pressure (Schultz and Nardin 1994).

The mechanical interlock theory implies that the physical structure of the adhesive interface influences adhesion. The mechanical interlock theory is shown in Figure 2.1.

Figure 2.1 has been removed due to copyright restrictions

Figure 2.1: Mechanical interlocking between adhesive and substrate (SpecialChem, n.d.)

The adherent is structured so that adhesives can flow into crevices or pores, but can not easily be pulled out (Filbey and Wightman 1988). Some studies have suggested that the effective submicroscopic penetration of adhesives in cellulose in wood occurs at a molecular weight of 1000 g/mol or less (Sellers 1994). In most cases adhesion can be enhanced by an increase in interfacial area resulting from increased surface roughness, (because wetting conditions permit penetration of the adhesive into pores and cavities). An increase in the effective surface area of the adherent also increases the number of primary and secondary bonds available to the adhesive. According to Davis and Shaffer (1994), surfaces with features on the order of tens of nanometers exhibit superior performance to those with features on the order of micrometers. Several factors contribute to this difference in performance. The larger-scale features are fewer in number and are generally smoother (even on a relative scale), so that interlocking is less effective. Larger-scale features also allow trapped air and surface contaminants to remain at the bottom of the troughs and pores. These unbonded regions limit joint performance by reducing both chemical and physical bonds and serving as stress concentrators (Davis and Shaffer 1994). The interlock theory was first proposed by MacBain and Hopkins (1925). Several years later experiments conducted by Borroff and Wake (1949) clearly showed that penetration of the adhesive into the adherent was the most important parameter for tested adhesive joints (Schultz and Nardin 1994). Borroff and Wake (1949), however, concluded that the mechanical interlock theory cannot be considered as universal, because good adhesion can occur between smooth surfaces.

The adsorption theory of adhesion, generally attributed to Sharpe and Schonhorn, is, according to Schultz and Nardin (1994), the most widely used approach in adhesion science at present. This theory postulates that primary and secondary

7

bonds formed at interfaces result in good adhesion. The secondary bonds are Van der Waals forces which include London dispersion forces, dipole-dipole, acid-base, and hydrogen bonding. The primary bonds are covalent or ionic bonds which form between the adherent and the primer and/or adhesive (Filbey and Wightman 1988). The typical strength of a covalent bond, for example, is of the order of 100 to 1000 kJ/mol., whereas those resulting from Van der Waals interactions and hydrogen bonds do not exceed 50kJ/mol. The formation of chemical bonds depends on the reactivity of both adhesive and substrate. Generally, the formation of an assembly goes through a liquid-solid contact step, and therefore the criteria for good adhesion become essentially those for criteria of good wetting, although this is a necessary, but not sufficient condition (Schultz and Nardin 1994).

Schultz and Nardin (1994) concluded that adhesion is a very complex field beyond the reach of any single model or theory. In practice, several adhesion mechanisms can be involved simultaneously. However, it is generally assumed that the adsorption theory defines the main mechanism exhibiting the widest applicability. It describes the achievement of intimate contact and the development of physical forces at the interface. This is a necessary step for interlocking, inter-diffusion, and chemical bonding mechanisms to occur subsequently, further increasing adhesive strength (Schultz and Nardin 1994).

2.3. Types of Adhesives

The process of bonding wood materials with glue has been practiced since the early periods of civilization. Examples of glued wood materials exist which are thousands of years old, for example scarf-jointed wooden chariot wheels and decorative, thin-veneer-covered artifacts from the Pharaonic periods of Egypt (Sellers 1994). The adhesives examined in this study can be used for bonding wood, but they can be used for other purposes as well. The development of adhesives has shifted away from stiff, brittle adhesives towards ductile products. According to Jordan (1989) this shift has occurred mainly due to the susceptibility of the former adhesives to fatigue caused by dynamic load. The development of ductile adhesives is particularly beneficial for adhesives used in wood composites such as glulam, because it allows the wood to move in its dimension without putting too much stress on the gluline.

8

2.3.1. Epoxy Adhesive

In the nineteen thirties Schlack of I.G. Farben (today BASF) patented polyglycidyl ethers of polyphenols, including diphenylpropane (DPP). As mentioned by Potter (1970), 95% of epoxide resins were once diglycidyl ethers of DPP. Today most of the epoxide resins are made by the interaction of epichlorohydrin (ECH) and diphenylpropane (DPP) also called bisphenol-A (Kollek 1988, Goulding 1994) (Figure 2.2).
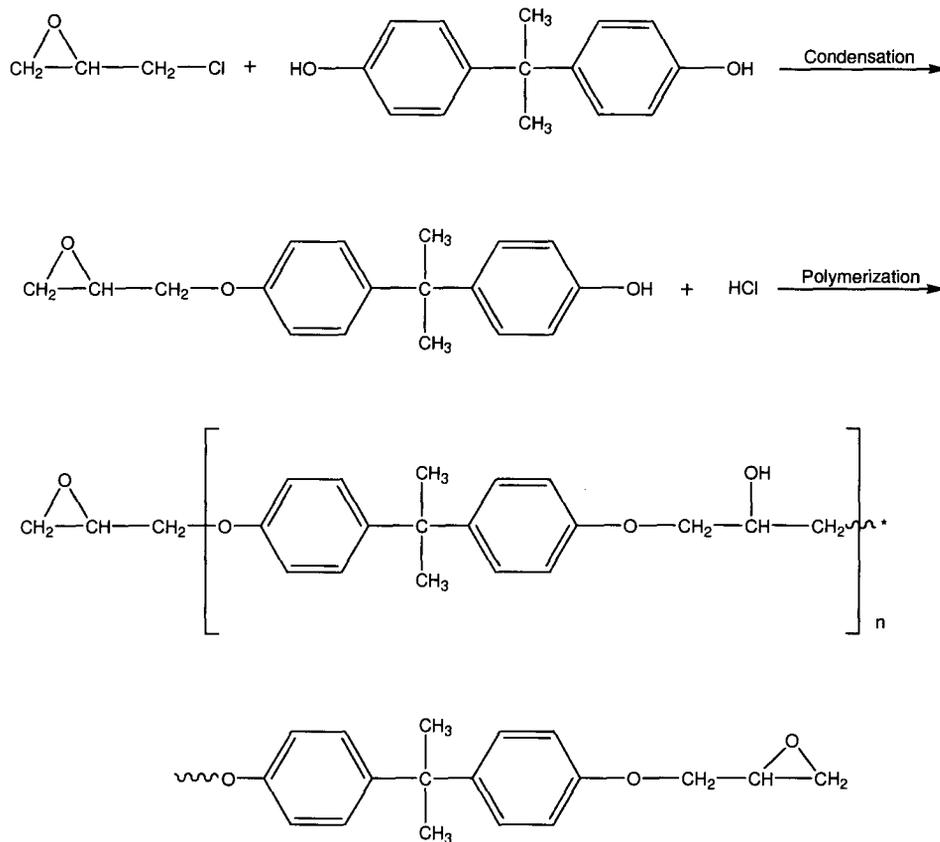
Figure 2.2: Chemical structure of epoxide resin derived from DPP and ECH

Goulding (1994) mentioned that epoxy resin derived from DPP and ECH is capable of reacting with various products, or itself, to form a solid, infusible product of considerable strength. The reaction with itself, as a result of homopolymerization, is typical of catalyzed cross-linking. Under the external cross-linking process, with the presence of hardeners, the oxirane group reacts with active hydrogen available e.g. in amines, and amides (Goulding 1994). The external cross-linking is shown below in Figure 2.3.
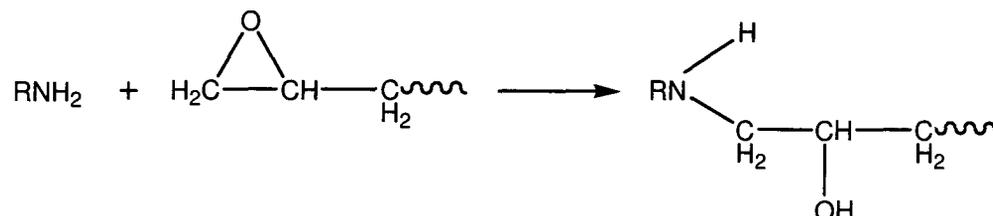
This product can react with an additional epoxide group to continue the cross-linking process
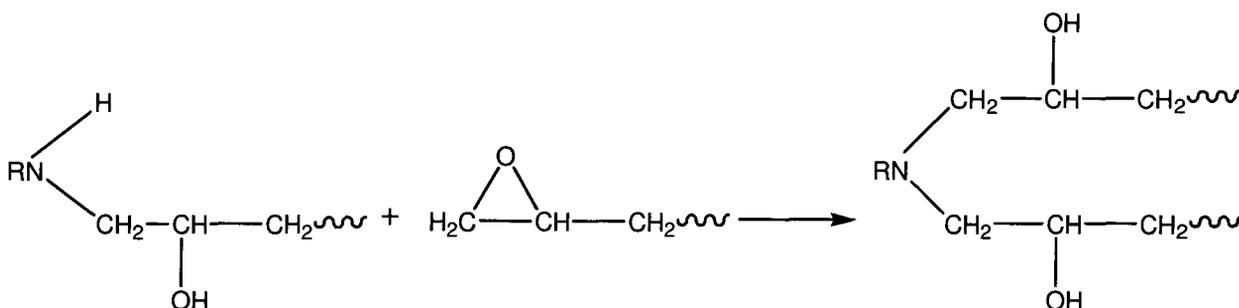
Figure 2.3: External cross-linking of epoxide resin with amine hardener (primary amine group)

The wide and increasing use of epoxy resins in industry, despite the relatively high cost of manufacturing them, is according to Paul and his colleges (1979) due to their unique combination of properties. Furthermore, Paul et al. (1979) mentioned that their properties such as good molding characteristics are due to the absence of volatile by-products and low shrinkage during cure, and the consequent minimization of internal stresses. These attributes give epoxy resins high mechanical properties. Paul et al. (1979) pointed out that the cured resins have high adhesive strengths due mainly to the generation of polar hydroxyl groups during cure, and they possess high electrical insulation and good chemical resistance. These properties of epoxy adhesives were

also reported by Petrie (2007). As suggested by Paul et al. (1979) many of these properties can be modified by blending resin types, selecting curing agents, or using fillers that confer a versatility on epoxy resins that is not found in other thermosetting systems. According to Davis and Shaffer (1994) epoxy adhesives are also used due to their greater toughness, and lower temperatures and pressures required during cure. Water thinnable epoxy systems are potentially capable of being used as wood adhesives and they form strong durable joints. The very slow attainment of maximum joint strength, however, may be a limiting factor for certain applications (Mynott and Van der Straeten 1984).

The extent of cross-linking of an adhesive describes the degree of cure. The nature of the resin molecules between cross-links and the nature of the curing agent determine the properties of the cured material (Potter 1970, Kollek 1988). To obtain the most favorable properties in any cured resin it is important to achieve maximum cross-linking. Infra-red spectra taken at various times during the curing process of epoxy adhesives have shown a loss of epoxy and an increase in hydroxyl concentration (Figure 2.4).

Figure 2.4 has been removed due to copyright restrictions

Figure 2.4: FTIR spectra of epoxy polymer before and after a "standard" curing schedule; a, freshly mixed adhesive; b, after being cured at 160 ℃ for 2.5h (Hon 1994)

The extent of hydrogen bonding in cured epoxide networks has been investigated by Harrord (1963). He concluded that in the temperature range of 30-200 °C the hydroxyl group is extensively involved in hydrogen bond formation. Paul et al. (1979) stated that 'the cured resin has high adhesive strengths due mainly to the generation of polar hydroxyl groups during cure'.

Amstock (2001) pointed out that epoxies are thermosetting and can be defined as any molecule containing more than one a-epoxy group capable of being converted to a thermoset form. The epoxide group is a three-membered oxide ring. The resin compounds contain on average more than one epoxide group per molecule, and they are polymerized through these epoxide groups, using a cross-linking agent (also called a curing agent or hardener). Epoxy resin is mostly used in the cured state when all epoxide have reacted; in the uncured non-cross-linked state they are of limited utility. With increasing degree of polymerization the resins become solids of increasing melting points (Potter 1970, Amstock 2001). The characteristic physical, chemical, and electrical properties of the cured resin all stem from the basic molecular structure of the polymerized resin. Important factors at the molecular level which determine these properties are: 1, the extent of cross-linking, i.e., the degree of cure; 2, the cross-link density; 3, the nature of the resin molecule between cross-links; and 4, the nature of the curing agent molecule (Potter 1970). Comyn et al. (1979) suggested that during curing the epoxide ring may get opened to produce either alcohol or ether units. These groups probably contribute to both the adhesion and water absorption associated with epoxides. Both of these chemical groups are hydrophilic. According to Althof (1981) epoxy nylon adhesive bonded joints suffer a decrease of strength when they are exposed to a wet, hot, climate (Althof 1981).

According to Paul et al. (1979) the versatility of epoxy adhesives can be improved by blending them with different resin types, selecting curing agents, or using fillers. Such versatility is found in other thermosetting systems.

2.3.2. Emulsion Polymer Isocyanate (EPI) Adhesive

Poly vinyl acetate (PVAC) was used as a solvent-based adhesive in the 1930s, and later as a hot melt, but it did not become commercially important until its use in the 1940s as an emulsion adhesive for paper and wood. Today, in emulsion form as white glue, it is the world's most widely used thermoplastic adhesive (Keimel 1994). According to Sellers (1994) PVAC adhesive impart relatively high bond strength, cures quickly and forms colorless bond-lines. They are free from the environmentally questionable compound formaldehyde. PVAC is compatible with plasticizers, wetting agents and other additives, which allow different formulations to be created. Increasingly, copolymer forms are offered commercially to decrease stress-related creep and to enhance exterior durability (Sellers 1994).

At the end of the last century EPI adhesives were developed based on PVAC dispersions containing isocyanate hardener. These were able to form some water-resistant bonds, unlike PVAC (Krystofiak, Proszyk, and Mariusz 2003, Dynea, n.d.). Sellers (1994) mentioned that polymeric diisocyanate (PMDI) can continue to cross-link by reaction with itself in the presence of absorbed moisture and that PMDI is used as a catalyst in vinyl emulsions. Krystofiak, Proszyk, and Mariusz (2003) found that the glue lines formed from EPI adhesives have high thermal and water resistance, which is, to some extent, influenced by type and amount of isocyanate hardener. EPI can be classified as a thermoplastic adhesive with properties very close to other thermosetting adhesives. EPI adhesives can be formulated to alter their water resistance, curing speed, strength and viscosity to suit different substrates. EPI adhesives are cold-setting with very good adhesion to difficult-to-bond hardwoods and they are also fast curing even at high wood moisture content (Dynea, n.d.). EPI adhesives have not been used extensively for glulam beams.

2.3.3. Melamine Adhesive

Melamine formaldehyde resins were commercially used for the first time in the 1930's (Chugg 1964). Melamine reacts with formaldehyde to form methylol melamine (hexamethylolmelamine), as shown in Figure 2.5. Two to six methylol groups can be held by a melamine molecule. Methylol melamine reacts by condensation to form hydrophobic intermediates, with splitting of water and formaldehyde (Pizzi 1994, Chugg

1964), see Figure 2.6. Garnier et al. (2001) demonstrated that methylene ether bridges (-CH₂OCH₂-) occur, which rearrange themselves with relative ease to form methylene (-CH₂-) bridges with liberation of formaldehyde. The final curing process transforms these intermediates into an insoluble cross-linked MF resin through the reactions of amino and methylol groups (Pizzi 1994, Chugg 1964, Figure 2.7). According to Pizzi (1994) fully cured melamine resins possess high hardness and abrasion resistance. They are not flammable and are resistant to chemicals.
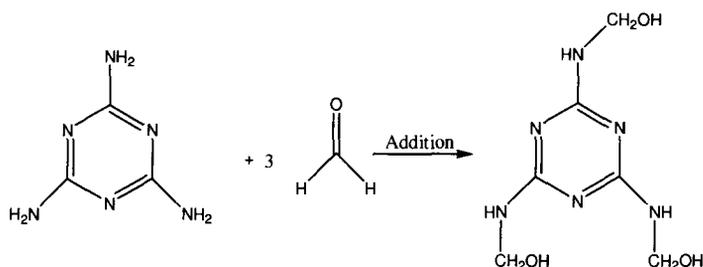
Figure 2.5: Reaction scheme of melamine and formaldehyde
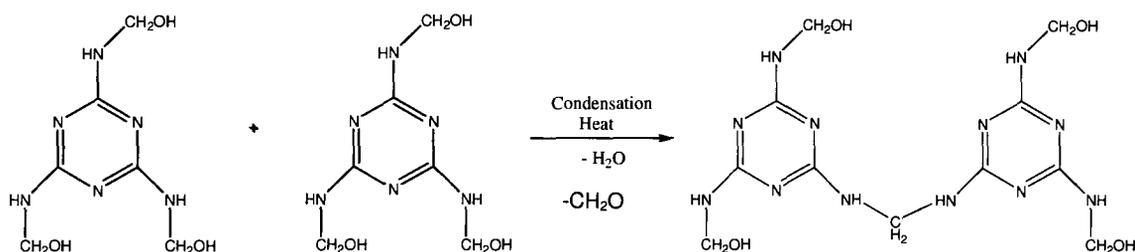
Figure 2.6: Reaction of methylol melamine by condensation to form intermediates
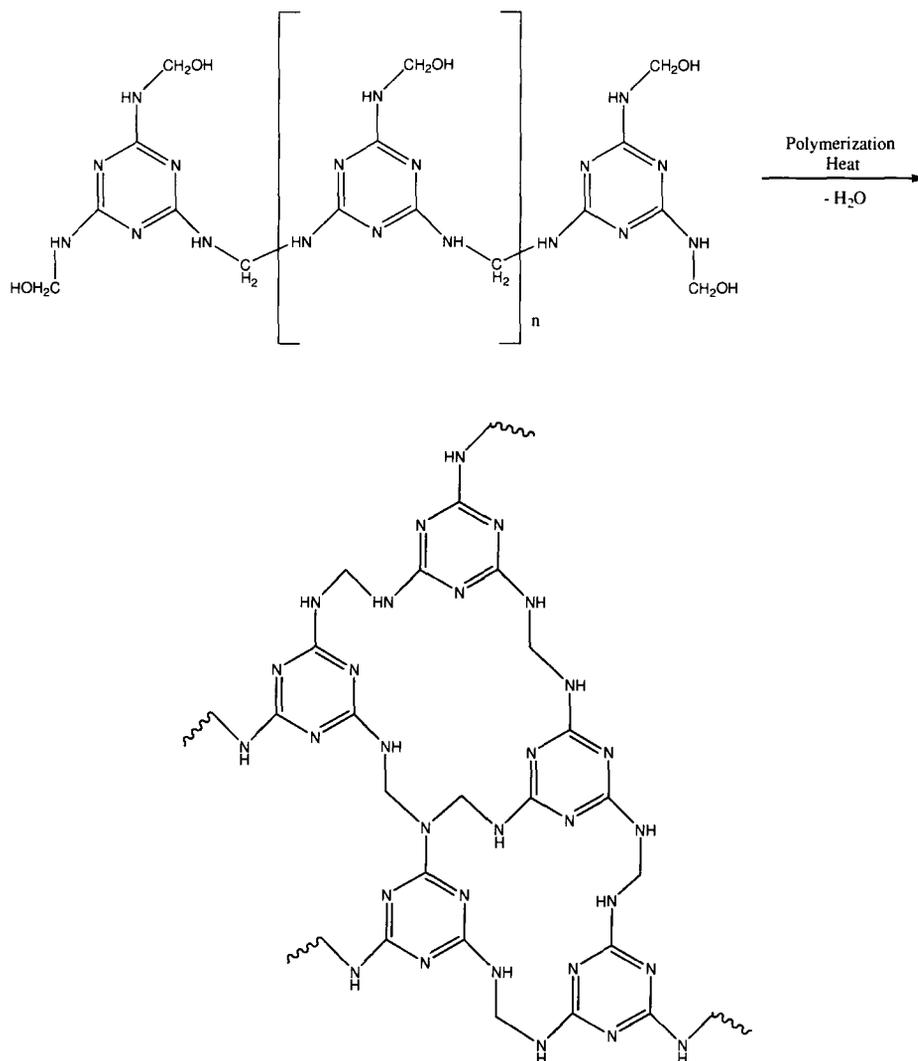
Figure 2.7: Final curing process through reaction of amino and methyl groups

Pizzi (1994) mentioned that melamine-formaldehyde and melamine urea formaldehyde resins are among the most widely used adhesives for wood panels, both in exposed and semi-exposed conditions because they are more resistant to hydrolysis than urea formaldehyde adhesives.

2.4. Degradation of Polymers/Adhesives

Polymers can be degraded chemically by photo-oxidation, thermal decomposition and oxidation, hydrolysis, or attack by pollutants (Davis and Shaffer 1994, Stevens 1999). Jordan mentioned that chemical degradation processes can have physical origins such as those resulting from heat and light (Jordan 1989).

Degradation is an irreversible process, and in general it involves chemical alteration of the polymer caused by the service environment. Frequently, but not always, these changes reduce the performance of polymeric materials (Akmal and Usmani 2000). Akmal and Usmani (2000) stated that polymers, whether man-made or natural, often lose their properties such as appearance, mechanical strength, and overall integrity when they are exposed to UV light.

Some polymers degrade more rapidly than others (Akmal and Usmani 2000). The rate of degradation depends on a number of variables that can be grouped into three categories: environment, material, and stress (Davis and Shaffer 1994). Stevens (1999) stated that the lower the molecular weight, the more rapidly the polymer degrades. Nguyen and Rogers (1988) proposed that mechanical stress on melamine-acrylic coatings on an aluminum substrate accelerated degradation. Hence, with increasing stress the loss of melamine triazine rings and the rate of formation of hydroxyl and amine groups increased. The acceleration of degradation was considered to be due to enhanced oxygen accessibility and, possibly, the more direct effects of stress on the reaction mechanism and its micro reversibility (Nguyen and Rogers 1988).

Extensive work on the degradation of many polymers has been undertaken and key degradation reactions have been identified. According to Akmal and Usmani (2000), it is possible from these sets of reactions, to accurately anticipate the major causes of degradation of any new or modified polymer. To investigate the degradation of an adhesive used to bond two materials together, however, it is important to focus on the system adhesive and substrate and not only on the adhesive itself (Jordan 1989).

2.5. Weathering of Adhesives

Many polymers are prone to photo-chemical degradation, caused by ultra-violet solar radiation and atmospheric oxygen, which lead to chain scission of the polymer backbone (White and Turnbull 1992). Such chemical reactions may be accelerated by elevated temperatures and by stress, as mentioned above. Stress may be applied externally or can result from a temperature gradient or difference in thermal expansion coefficients at different locations in the polymer (White and Turnbull 1992).

The weathering of polymeric materials is generally due to a complex interaction of the effects of all environmental factors, including solar radiation, moisture, heat, atmospheric pollutants, and others. Some of them only contribute to degradation through their effects on secondary reactions that follow bond breakage (Searle 2000).

2.5.1. Solar Radiation/Heat

Solar radiation, particularly ultraviolet (UV) radiation, is mainly responsible for limiting the lifetime of materials exposed to the environment (Osawa 1983, Searle 2000). UV radiation has enough energy to initiate degradation processes by directly breaking organic chemical bonds. However, light that is not absorbed can not cause any damage Searle (2000).

Approximately 8% of the solar radiation on earth is in the ultraviolet range (280 - 400 nm). Its photochemical effect is decisive in the degradation of polymers because of its higher quantum energy. The photon energy of solar radiation is inversely proportional to its wavelength (I):

$$(I): E=2.86*10^4/\text{lambda}$$

where, E = energy of a photon (kcal/mol) and λ wavelength (nm)

The cut-off for short-wave UV radiation at the earths surface is determined by the UV absorption of the ozone layer in the atmosphere (Searle 2000). Even long-wave UV radiation, however, may causes photochemical reactions that can modify the character of polymers. The partial depletion of ozone may lead to the enhancement of shorter wavelength solar radiation reaching the earth. This may lead to acceleration of photodegradation of polymeric materials, resulting in a decrease of useful lifetimes for

17

polymers exposed outdoors (Torikai 2000). Photosensitization of polymers to long-wave radiation caused by dyes, pigments, or processing additives may also reduce the lifetimes of polymers exposed to solar radiation Kockott (1988). The spectral absorption properties of polymers are determined by their chemical structure. Pure types of aliphatic-type polymers (e.g. polyethylene, polypropylene, PVC), and others, are not capable of absorbing terrestrial solar radiation. The effect of solar radiation on these polymers is due to the presence of UV-absorbing impurities and thermal oxidation products introduced during polymerization and processing. Furthermore, hydro peroxides and carbonyl groups in polymer chains increase the susceptibility of polymers to photodegradation.

Visible radiation absorbed by colored materials can cause deterioration of polymers (including color changes). Visible radiation, between 400 and 800 nm, generally makes up 52% of total solar radiation. It also contributes to heating (Kockott 1988, Searle 2000). Over 40% of solar radiation has wavelengths longer than 800nm, which is not visible to human eyes, e.g. infrared (IR) radiation. It has a higher irradiance than UV and visible radiation (Williams 2005). As a result, the temperature of materials exposed to IR radiation rises automatically (Kockott 1988). Kockott (1988) found that a temperature rise at the surface of an organic material will increase the rate of chemical reactions, initiated by UV radiation. Davis and Shaffer (1994) concluded that elevated temperature conditions tend to degrade adhesive joint strength at a faster rate. An approximate rule drawn from reaction kinetics states that a temperature increase of 10 °C will approximately double reaction rates. Therefore heat plays a major role in the ageing of polymers. In amorphous and partially crystalline polymers, the glass transition temperature plays a role, since the mobility of the chains and radicals increases above the glass transition temperature and, simultaneously, oxygen diffusion occurs more rapidly (Kockott 1988).

UV energy incident upon the surface of a polymer will penetrate into the surface to an extent dependant upon its incident intensity. As the UV energy penetrates further into the sample, its intensity becomes increasingly attenuated due to polymer absorption (Keene et al 2001). The intensity of radiation absorbed by a material obeys Lambert-Beer's law; which governs the relationship between absorbance and penetration depth, absorbtivity, and concentration of material (Osawa 1983). The

absorption of light equals a constant multiplied by the UV absorber concentration multiplied by the path lengths (Horsey 1994). As a result the magnitude of chemical change to polymer exposed to solar radiation decreases as a function of depth (Keene et al. 2001).

2.5.1.1. Photodegradation of Adhesives

Photodegradation is defined as a change in surface chemistry caused by UV radiation, which may result in discoloration and, following prolonged UV exposure, to losses in mechanical integrity (Muasher and Sain 2006). Stark and Matuana (2006) pointed out that the physical result of photodegradation of polymers is surface cracking and loss in strength and stiffness. Ranby and Rabek (1975) mentioned that in most mechanistic studies photochemical reactions are carried out in gas or liquid phase, and rarely in the solid phase, whereas in most empirical studies of the susceptibility of polymers to degradation expose materials as solids.

The initial step involved in the photodegradation of polymers is photo-absorption at a specified wavelength, depending on the polymer structure and the presence of impurities (Torikai 2000). According to Ranby and Rabek (1975) most polymers only contain molecules with C-C, C-H, C-O, C-N and C-Cl bonds and hence are not expected to absorb light of wavelengths longer than 190 nm. Furthermore, Searle (2000) mentioned that only short wavelength photons absorbed by the main structural components are capable of causing severe degradation, such as bond scission. Free radicals, however, are formed after polymers are irradiation with UV light of wavelengths > 300nm (Ranby and Rabek 1975). Ranby and Rabek (1975) and Horsey (1994) suggested that chromophores and small quantities of impurities are responsible for the absorption of light quanta in polymers. Adhesives can degrade via the photo-oxidative pathway and/or photolytically. In the latter, polymers which are chromophores absorb UV light directly without first undergoing oxidation reactions. Examples of these polymers are aromatic polyurethanes or polyesters (Horsey 1994), and lignin in wood. Only a small portion of the radiation absorbed by a polymeric material causes photochemical changes. Other absorbed radiation is eliminated in harmless ways. According to Searle (2000) the activation spectrum of a material, is the point at which photochemical reactions occur, depending on the absorption properties of the material,

the spectral emission properties of the light source and the quantum efficiencies of the absorbed wavelength. The Grotthus and Draper's law states that photochemical reactions only take place, when molecules are excited to higher states via absorption of light quantum of sufficient energy. Therefore, the absorption of light is the indispensable first step in the initiation of photochemical reactions (Jellinek 1983, Ranby and Rabek 1975). Torikai (2000) pointed out the importance of finding out the wavelength sensitivity of a polymer; which means to clarify what reactions occur and which wavelength is responsible in order to develop an effective and appropriate protection system.

2.5.1.2. Factors Responsible for Photodegradation of Adhesives

Generally photodegradation processes in polymers exposed to light are very complex because different types of impurities, additives, or abnormal bonds in polymers absorb UV radiation (Torikai 2000). Industrially produced polymers contain a number of light-absorbing impurities produced in side-reactions during polymerization, processing, and storage. These impurities can be divided into two groups: Internal impurities containing chromophoric groups, such as hydroperoxides, carbonyls, unsaturated bonds, and catalyst residues; and external impurities, which may contain chromophoric groups. These may be traces of solvents, catalyst, and metals or metal oxides from processing containers and equipment. Compounds from polluted urban atmospheres and smog, and various additives may also act as photosensitizers.

Torikai (2000) mentioned that a range of other factors also influence the photodegradation of polymers. These include the molecular weight of the polymer and its distribution, the processing technique, the temperature maintained during processing, the mechanical tension during the preparation of the film, its density, the extent and distribution of crystallinity, the size of the crystallites, the structure at the surface of the film, the boundary region between crystalline lamella, any defects within the crystal cores and the orientation or mobility of the chains. Some of these factors will be discussed later on in this thesis.

2.5.1.3. Free Radical Generation

Akmal and Usmani (1994) stated that the origin of all the degradative processes in polymers following absorption of light is the initial bond-breaking reaction. Bond cleavage, to produce a free radical pair, can be induced by radiation energy (ultraviolet, gamma, x-ray, and electron beam), mechanical action (e.g. any type of shearing process extending the cohesive forces of the molecules such as stretching, grinding, milling, or sheeting), or heat (Horsey 1994, Akmal and Usmani 1994). Photooxidative degradation of polymers includes such processes as chain scission, crosslinking, and secondary oxidative reactions (Rabek 1987).

Under these circumstances, internal and or external chromophoric groups can produce low molecular radicals (R*) and or polymeric radicals (P*). Photon energy absorbed by a given chromophoric group can cause polymer dissociation into free radicals by energy transfer to another group (energy transfer process), or the energy can be accumulated at a given bond (by an energy migration process) (Rabek 1987).

In the presence of oxygen and in an extremely fast reaction molecular radicals and or polymeric radicals form peroxyradicals (ROO*) (Horsey 1994). Abstraction of hydrogen from a polymer molecule transforms the peroxyradicals into a hydroperoxide. This can further decompose to generate two new free radicals (RO*, HO*), which can initiate further reactions (Rabek 1987, Horsey 1994). This autocatalytic mechanism results in autooxidation and an increase in the number of free radicals available to initiate new degradation reactions. The general autooxidation scheme for hydrocarbons shown in Figure 2.8, represents the core reaction for hydrocarbon degradation (Horsey 1994) and is applicable to both wood and adhesive degradation.

21

Figure 2.8 has been removed due to copyright restrictions

Figure 2.8: Autooxidation scheme for polymer degradation showing the cyclic nature of the process (Horsey 1994)

Hydroperoxide can dissociate by thermolysis at temperatures above 100 °C and via a photolytic pathway under ambient temperatures. According to Klemchuck and Gande (1988) the latter is the major cause of photo-induced polymer degradation. Other photo-induced reactions can occur due to light absorption by trace levels of carbonyl impurities resulting from thermal degradation of the polymer (Horsey 1994).

Subsequent reactions of free radicals amongst each other can result in crosslinking; which is understood as the termination reaction (Rabek 1987). In general, termination mechanisms for free radical reactions are chain scission and cross-linking. The ramification of degradation of polymers via cross-linking includes hardening, skinning, gel formation, a decrease in tack, and an increase in viscosity. Degradation via chain scission results in softening, a viscosity decrease, an increase in tack, and a loss of cohesive strength. In addition to these physical changes, discoloration is also possible (Kockott 1988). According to Stark and Matuana (2006) chain scission can result in more chain mobility and secondary recrystallization. While cross-linking and chain scission are competitive mechanisms during UV degradation, cross-linking has been shown to be the preferred mechanism during accelerated weathering (Stark and Matuana 2006).

2.5.2. Water/Humidity

The effect of humid air on certain adhesives joints was first reported in 1964 (Kerr, MacDonald, and Orman 1970). Water is omnipresent in different states in the environment and it has a direct impact on polymers which are exposed to it (Kockott 1988). As Davis and Shaffer (1994) suggested, moisture is the cause of most environmentally induced bond failures. It can weaken or disrupt secondary (dispersion forces) bonds across the adhesive-adherent interface.

Kockott (1988) recommended differentiating between two models of action of water on organic materials. First there is the mechanical stressing of the material caused by swelling due to water uptake. Secondly, the chemical reaction of water with the polymer, as seen e.g. in hydrolysis; where water, oxygen and short wave radiation are responsible for free radical generation which can lead for example to chalking of some polymers. The latter was observed in TiO_2 (titanium oxide) pigmented coatings and plastics (Kockott 1988). Hydrolytic attack can also cause chain scission in some polymers, leading inevitably to deterioration in properties; which can occur unacceptably fast at elevated temperatures (White and Turnbull 1992). Water is especially aggressive at temperatures of 70 °C and higher. Even rather hydrophobic materials can be affected by water, as suggested by Jordan (1989).

Organic materials have a relatively low diffusion coefficient of 10^{-8} cm^2/s. In fact rapidly changing humidity conditions at the surface of polymers, results in less penetration of water into the material, and lower mechanical stresses. According to Kockott (1988) in a polymer with a diffusion coefficient of 10^{-8} cm^2/s, seasonal humidity fluctuations penetrate approximately 1.7 mm into the material. Kockott (1988) pointed out that water absorption capacity and diffusion coefficients are important factors that influence polymer ageing. Moisture can diffuse through the adhesive or the adherent (Moloney et al. 1981), or it can wick or travel along the interface where it can migrate via capillary action through cracks and crazes in the adhesive (Davis and Shaffer 1994). Once moisture is present, it can attack adhesive bonds by:

1. Plasticizing the adhesive
2. Swelling the adhesive and inducing concomitant stresses

3. Disrupting secondary bonds across adherent-adhesive interfaces

4. Irreversible altering the adhesive (e.g. hydrolysis, cracking, or crazing)

5. Hydrating or corroding the adherent surface

According to Davis and Shaffer (1994) plasticization of the adhesive, which depresses T_g (glass transition temperature) and lowers the modulus and strength of the elastomer, is of primary importance in moist environments. Plasticization of the adhesive may also allow disengagement from a micro-rough adherent surface to reduce physical bonding and thus reduce joint strength and durability. On the other hand it may also cause stress relaxation or crack blunting and improve durability (Davis and Shaffer 1994).

2.5.3. Oxygen

Atmospheric oxygen causes oxidation of polymer matrices and this effect is strongly accelerated by UV irradiation especially at elevated temperatures and by the presence of certain impurities that catalyze the oxidation process (Horsey 1994, Jordan 1989, Stevens 1999). Hydrocarbon-based adhesive formulations that contain double bonds are particularly susceptible to oxidation (Jordan 1989); whereas Stevens (1999) pointed out that tertiary carbon atoms are most susceptible to attack. Saturated polymers are degraded very slowly by oxygen, and the reaction is autocatalytic. Unsaturated polymers undergo oxidative degradation much more rapidly as a result of complex free radical processes involving peroxide and hydroperoxide intermediates (Stevens 1999). Stevens (1999) stated that singlet oxygen, whose concentration in the atmosphere is negligible (but there are several sources to produce it e.g. decomposition of ozonides), reacts with unsaturated carbon-carbon bonds to produce hydroperoxides. It is further known that polymers containing hydroperoxides have reduced photostability. This was confirmed by Williams (2005) who further mentioned that singlet oxygen quenchers could preclude the formation of hydroperoxides, thereby stabilizing wood against photodegradation.

Oxidative degradation can occur during the isolation, storage, compounding, and end use of polymers and adhesives. Also for most hydrocarbon polymers, as noted by

Carlsson (1990), photodegradation is not a function of their tendency to absorb light; rather it is a function of their susceptibility to oxidation. To prevent thermal oxidation reactions, antioxidants are used in adhesive formulations (Earhart, Patel, and Knobloch 1994); but Jordan (1989) suggested that antioxidants are not capable of stopping oxidation reactions completely. Turton and White (2001) mentioned that the reaction rate near the surface of a polymer exposed to UV is very high and most of the oxygen is consumed before it can penetrate far into the material. The most aggressive form of oxygen is ozone, for which special antioxidants have been developed (Jordan 1989, Stevens 1999). Nitrogen (N) has no significant affect on adhesives. The impact of other atmospheric air constituents such as sulfur dioxide and nitrogen oxide on the degradation of polymers has not been fully investigated (Jordan 1989).

Stark and Matuana (2006) found out that carbonyl growth shows a linear relationship with growth in surface oxidation. According to Dorn and Breuel (1992) the presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and, furthermore, that the material is vulnerable to further deterioration because such groups are photo-labile.

2.5.4. Pollutants

Industrial pollutants have a direct impact on the weathering of polymers without any interaction with other weathering factors. Laboratory experiments have shown that pollutants cause degradation of polymers (such as Nylon 6), even in the absence of UV radiation (White and Turnbull 1992). Nichols (2005) pointed out that atmospheric pollution can lower the pH of rainfall, leading to acid etching of coatings. However, significant loss of properties occurs only as a result of the combination of different weathering factors. For example sulfuric acid in combination with water and solar UV radiation is responsible for rapid fading (Kockott 1988). Some of the pollutants themselves are photolytic, leading to the generation of additional products that may cause degradation (White and Turnbull 1992). The common atmospheric pollutants in industrialized regions are sulphur dioxide, oxides of nitrogen and carbon, and ozone. There is significant synergy between their activity and photodegradation.

2.6. Weathering of Wood

Wood undergoes rapid surface degradation during exterior exposure due principally to the effects of light and water (Feist and Hon 1984). The term weathering describes the surface degradation that occurs when wood is used outdoors and above ground. As Feist and Horn (1984) pointed out weathering should not be confused with decay caused by fungi, which can extend deeply into wood and significantly reduce the strength of structural timber. Evans (2005) stated that microorganisms play a minor role compared to environmental factors in the degradative processes involved in weathering. According to Yusuf and co-workers (1995), the main factors that are responsible for the natural weathering of wood are solar radiation, especially the UV component, moisture in its different states, heat and atmospheric gases. They emphasized that the UV portion of the solar spectrum is more energetic than visible light and most effective at causing degradation of wood (Yusuf et al. 1995). Visible light is also involved in weathering, according to Derbyshire and Miller (1981). Nearly 30% of softwood is composed of lignin, which contains numerous chromophores that efficiently absorb UV radiation (Heitner 1993). Water washes degraded products such as lignin and hemicelluloses from weathered wood, but cellulose remains on the surface because some of its degradation products are less water soluble (Muasher and Sain 2006). Feist (1990) mentioned that the most obvious features of weathered wood are its grey coloration, rough surface texture and presence of checks. Extractives are leached from weathered wood surfaces and this, in combination with loss of lignin makes the surface more hydrophilic (Williams 2005). Wood is naturally a hydrophilic material and wood cell walls swell when they absorb water. This facilitates deeper light penetration and provides sites for further degradation (Stark and Matuana. 2006). The effects of weathering are superficial in nature and are confined to the upper 2-3 mm of wood, except for checks which can extend more deeply into wood. Kataoka, Kiguchi, and Evans (2004) found that the first 75 μm thick layer of wood absorbed 90% of UV light (350 nm), and the first 220 μm thick layer absorbed 90% of visible light (420 nm). One percent of UV and visible light, however, was capable of penetrating wood to depths of 150 and 440 μm, respectively. It is generally understood that low density earlywood degrades more rapidly than denser latewood, but it is not clear to what depths light is still photo-chemically active in wood (Kataoka, Kiguchi, and Evans 2004). Hon and Feist

(1981) stated that crystalline regions of cellulose are impervious for UV light and they suggested that this might explain why denser late wood degrades less rapidly than early wood.

2.6.1. Photodegradation of Wood

Photo-oxidation of lignin refers to a process where lignin undergoes chemical modifications such as bond cleavage, and hydrogen abstraction resulting in radical formation, creation of peroxides with oxygen and finally its decomposition and the production of colored and hydrophilic by-products, so called chromophores. These modifications induce surface property changes such as discoloration, increased water sensitivity followed by hydrolysis, leaching and cracking (Hon 1991). Lignin is reported to absorb UV light with a maximum at 280 nm and decreasing absorption extending beyond 380 nm into the visible region of the solar spectrum (Kalnins 1966). Generally, photodegradation is triggered by the absorption of UV light by lignin and the formation of free radicals as suggested by Yusuf and his co-workers (1995). Lignin has various reactive groups that react with light to form free radicals (Stark and Matuana 2006, Hon 1981).

The mechanisms of photo-oxidation of lignin (Figure 2.9) are only partially understood and documented (Leary 1994). It is generally accepted that at least four reaction pathways are involved in the degradation of lignin: (1) direct absorption of UV light by conjugated phenolic groups to form phenoxyl free-radicals; (2) abstraction of phenolic hydrogen as a result of aromatic carbonyl triplet excitation to produce a ketyl and phenoxyl free-radical (Kringstad and Lin 1970); (3) cleavage of non-phenolic phenacyl-α-O-arylethers to produce phenacyl phenoxyl free-radical pairs (Gierer and Lin 1972), and; (4) abstraction of benzylic hydrogen of the α-guaiacylglycerol-β-arylether group to form ketyl free-radicals which then undergoes cleavage of the β-O-4 ary-lether bond to produce an enol and phenoxyl free-radical (Scaiano, Netto-Ferreira, and Wintgens 1991). The enol then tautomerizes to a ketone. Alkoxyl and peroxyl free-radicals produced from the reaction of oxygen and lignin free-radicals react with the phenoxyl free-radical formed to produce colored chromophores, e.g. quinoides, aromatic ketones, aldehydes, and acids as photo-degradation products (personal communication 2007, Schaller).
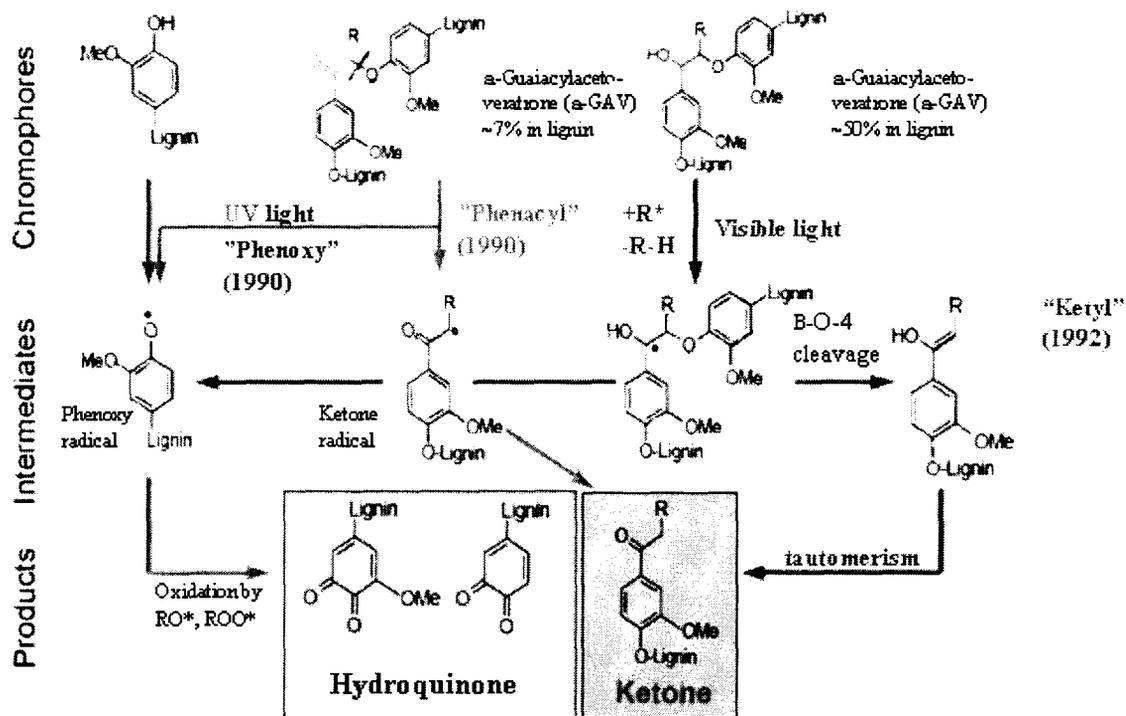
Figure 2.9: Pathways of lignin photo-oxidation

As described by Derbyshire and Miller (1981) there are two mechanisms for the photodegradation of wood, direct photolysis of lignin (as described above) and photosensitized degradation of cellulose. Photolysis involves the rupture of covalent bonds in lignin and extractives (Derbyshire and Miller 1981). The rate at which wood cellulose cleaved is reported to be dependent on the wavelength of the incident light. Wavelengths less than 280 nm increase the rate of photolysis, but the rate is slower on exposure to wavelengths longer than 340 nm (Evans et al. 2005). Photo-sensitized degradation is the most likely explanation for the breakdown of cellulose (Derbyshire and Miller 1981). Also Hon (1981) suggested that UV light absorbed by lignin helped to degrade cellulose by energy transfer.

2.7. Photo-stabilization

Potter (1970) suggested that an understanding of the mechanism by which a polymer deteriorates may lead to new approaches to stabilization. Light stabilizers are additives to polymeric materials which prevent photodegradation or crosslinking caused by UV light (Ranby and Rabek 1975, Rabek 1987). A number of books and reviews discuss photostabilization mechanisms and photostabilizer properties. As pointed out by Rabek (1987), 'the practical problem in the study of photostabiization of polymers is a voluminous patent literature on these products, whereas a highly fragmented and often contradictory scientific literature has attempted to answer mechanistic questions'. However, only a few classes of photostabilizers are of commercial significance (Ranby and Rabek 1975).

Any degradation by UV radiation is close to the surface of a material because the attenuation of light with increasing substrate depth. Therefore, the concentration of UV absorbers should be highest at the surface (Rabek 1987). In general, the concentration of stabilizers added to the materials is a function of the thickness of the substrate. The thinner the polymer, the higher the concentration of UV absorber needed to provide adequate protection. In a thin film the surface layer is a much larger fraction of the total film volume than it is for a thick film. Therefore, the surface layer plays a more important role in affecting the total properties of the film (Rabek 1987). Or as Decker (2001) stated 'the radiation filter effect of UVA is much greater when the entire light stabilizer is concentrated in a thin layer on the materials face exposed to sunlight'. The radiation filtering effect of UVA increases exponentially with its concentration according to the Lambert-Beer law (Decker, Zahouily, and Valet 2001). Also any type of additive (photostabilizer, antioxidant, thermal stabilizer, etc.) must be evenly distributed within the polymer, which requires it to be compatible with the polymer. Stabilizers are usually more compatible with the amorphous part of a polymer, and may be excluded from semi-crystalline polymers. Furthermore, oxygen diffusion is higher in the amorphous region. It is clear that much of the photooxidative reaction and stabilization occurs in the amorphous polymer region, and high stabilizer concentrations are required there (Rabek 1987).

Nowadays, two general classes of light stabilizers are mainly used to protect polymers from photodegradation, UV absorbers (UVA) and hindered amine light

stabilizers (HALS) (Horsey 1994, Rabek 1987). It is known that the use of HALS with a UV absorber provides excellent stabilization in many polymer compositions according to Berner and Rembold (1981). Muasher and Sain (2006) have shown a synergetic effect of UV absorber in combination with HALS in the UV protection of low density polyethylene. Also Decker, Zahouily, and Valet (2001) stated that the combination of UVA and HALS has a pronounced stabilizing effect on the photodegradation of methoxylated melamine, trifunctional isocyanate and polyurethane coatings. It is understood that UV stabilizer operate most efficiently by energy transfer from excited chromophores in the polymer, rather than solely by a screening mechanism (Ranby and Rabek 1975).

Another additive, which is used to protect adhesives from oxidation when they are subjected to high temperatures during processing and compounding, is an anti-oxidant. These only provide limited protection against UV-initiated oxidation (Horsey 1994).

2.7.1. UV Absorbers (UVA)

UV absorbers must fulfill certain requirements. They have to absorb strongly in the UV region (290 to 400 nm) and they need a sharp cut-off in the visible region (>400nm), so as not to color the polymer. They also must be quite photo-stable and dissipate the photoexcitation energy in a harmless way (Horsey 1994, White and Turnbull 1992, Renz 2001). Furthermore, Horsey (1994) explains that UV absorbers are more effective in protecting thick polymers than thin films, for reasons that are discussed above. This explains why UV absorbers are widely added to sealants but have limited efficacy in adhesive films, where typical thickness may be about 0.025mm. Decker, Zahouily, and Valet (2001) pointed out that UV absorbers also need to have the longest possible lifetime besides their good photostability. Furthermore he mentioned that the light stability of a UVA is not only dependant on its chemical structure, but also on the type of polymer it is applied to. The lifetime of an UVA is increased by the addition of HALS radical scavenger, because it helps the UVA to remain in the protective film, thus ensuring a long-lasting filtering effect (Decker, Zahouily, and Valet 2001). Information on the spectral response of a polymeric material to the source of radiation to which it will be exposed under use conditions is important in the

development of stabilizer systems to prolong its lifetime. The activation spectrum determines the wavelengths in the exposures source that are harmful to a specific material and thus the type of UV absorber needed for optimum screening protection (Searle 2000). The effectiveness of a UV absorber at protecting a material depends on its ability to compete with the polymer in absorbing actinic wavelengths. Different spectral regions may be responsible for the various types of degradation such as yellowing, loss in impact strength, and bleaching, as shown with ABS, polyethylene, and polysulfone exposed to borosilicate-glass filtered xenon arc radiation (Searle 2000).

Classes of UV absorber include salicylate, cyanoacrylate, malonate, oxanilide, benzophenone, s-triazine and benzotriazole (Renz 2001). From a technical point of view the hydroxyphenyl-benzotriazoles and hydroxyphenyl-s-triazines are the most important classes of UVA (personal communication 2006, Krause).

2.7.1.1. Hydroxyphenyl-benzotriazole

Benzotriazole UV absorbers are particularly useful for protecting polymers because of their increased photostability in comparison to other UV absorbers (Renz et al. 2001). However, Renz and colleges (2001) reported that there is a need for a benzotriazole that is highly soluble and provides added protection in the 350 to 400 nm region of the ultraviolet spectrum. The chemical structure of a hydroxyphenyl-benzotriazole is presented in Figure 2.10.
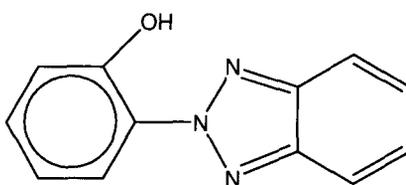
Figure 2.10: Chemical structure of hydroxyphenyl-benzotriazole

Ranby and Rabek (1975) mentioned that hydroxyphenyl-benzotriazole may form internal hydrogen bonds (Figure 2.11), as in the case of hydroxybenzophenones. Their photostabilization mechanism is also considered to be rapid tautomerism in their excited states.
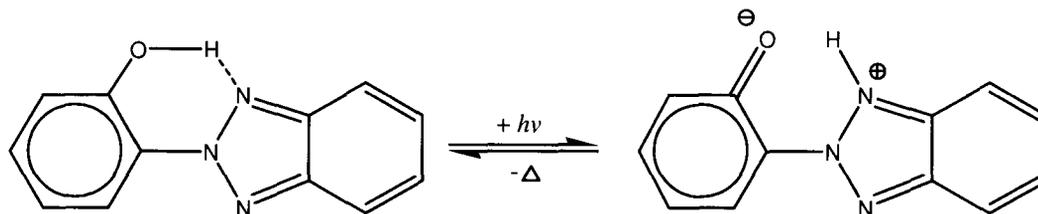
Figure 2.11: Internal hydrogen bond formation and tautomerization in a hydroxyphenyl-benzotriazole

2.7.1.2. Hydroxyphenyl-s-triazine

The mechanisms by which hydroxyphenyl-s-triazine UV absorbers stabilize polymers are similar to those of hydroxyphenyl-benzotriazoles. The chemical structure of hydroxyphenyl-s-triazine is shown in Figure 2.12.
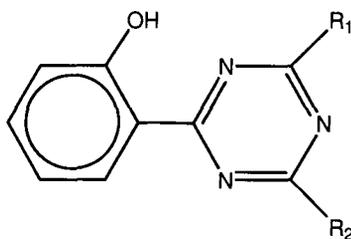
Figure 2.12: Chemical structure of hydroxyphenyl-s-triazine

2.7.2. Hindered Amine Light Stabilizers (HALS)

The second most important type of light stabilizer, HALS, provides stability to polymers and can function in thin films or on sample surfaces. Unlike UVA, HALS don't absorb UV radiation and therefore they have no effect on the incident light. The protective mechanisms of HALS involve the destruction of unstable and radical initiating hydroperoxides and scavenging free radicals before they can be involved in propagation reactions (Horsey 1994, White and Turnbull 1992). HALS were developed on an industrial scale during the 1980's. According to Rabek (1987) the simplest model compound for a HALS is 2,2,6,6-tetra-methyl-piperidine.

2.7.2.1. 2,2,6,6-Tetra-methyl-piperidine

It is generally accepted that hindered piperidine produces hindered piperidinoxy radicals during uv irradiation in the presence of oxygen (O_2) and free radicals (R*) as shown in Figure 2.13.
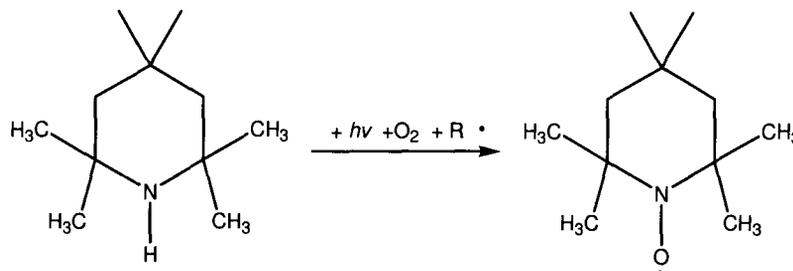
Figure 2.13: Formation of hindered piperidinoxy radicals from hindered piperidine

Piperidinoxy radicals belong to the class of stable organic free radicals and their formation mechanism is not fully understood. Their photostabilization mechanism and its kinetics are complicated because different piperidine derivates are participating in stabilization reactions and they are still being investigated (Rabek 1987, Horsey 1994). Nonetheless, Horsey (1994) pointed out that the primary protection mechanism of HALS involves free radical scavenging and hydroperoxide decomposing.

2.7.3 Antioxidants

Earhart, Patel, and Knobloch (1994) mentioned that antioxidants are used to inhibit degradation as a result of thermal oxidation. Ranby and Rabek (1975) classified antioxidants into two groups according to their protection mechanisms: 1, kinetic chain breaking antioxidants or primary antioxidants; 2, peroxide decomposers or secondary antioxidants. The primary antioxidants inhibit oxidation via a rapid chain-terminating reaction. Stabilization is achieved through proton donation from the –OH group of the primary antioxidant to a peroxy or alkoxy radical (Earhart, Patel, and Knobloch 1994). The performance of primary antioxidants can be improved by the use of secondary antioxidants as suggested by Earhart, Patel, and Knobloch (1994). The latter do not act as radical scavengers but they undergo redox reactions with hydroperoxides to form non-radical, stable products. Secondary antioxidants are generally used exclusively in combination with primary antioxidants (Earhart, Patel, and Knobloch 1994).

2.8. Weathering of Wood Polymer Composites

The photodegradation of wood and plastic separately are well documented in literature (Muasher and Sain 2006), but the photodegradation of blends of wood and polymers has received little attention.

2.8.1. Wood Plastic Composites (WPC)

It has been estimated that between the years 2004 and 2009, wood plastic decking will grow by 23% annually; this is mainly due to the fact that compared to other decking products wood plastic decking promises lower maintenance and greater durability (Stark and Matuana 2006).

Weathering resistance of WPC is generally poor despite claims to the contrary. Kiguchi et al. (2000) point out that discoloration, chalking and dimensional change caused by exterior exposure are major problems for the use of wood plastic composites outdoors. The color changes and losses in mechanical properties of wood plastic composites exposed to accelerated weathering conditions were examined by Muasher and Sain (2006), and Stark and Matuana (2006). Muasher and Sain (2006) mentioned that the photodegradation of wood plastic composites is complicated because each component, namely wood and plastic, may degrade via a different mechanism. Experiments have shown that both wood and plastic caused discoloration (whitening) of the composite. Dark pigments improved color stability, however, chalking on the surfaces of wood plastic composites still occurred (Kiguchi et al. 2000). Also Stark and Matuana (2006) pointed out that exposure of wood plastic composites to UV radiation can result in changes in both the polymer matrix and the wood component. Further they mentioned that wood plastic composites experienced much less color changes when exposed to UV (xenon arc type) alone. The majority of losses in mechanical properties during weathering were caused by moisture effects; in addition to the acceleration of oxidation reactions caused by water (Stark and Matuana 2006). The water also washed away the degraded polymer layer and removed wood extractives. The swelling of the wood fiber created micro-cracks in the composite matrix which facilitated deeper penetration of light (Stark and Matuana 2006).

2.8.2. Glulam Beams

The movement away from solid wood to engineered wood products for construction has increased the consumption of adhesives (Frihart 2005). Given the weight of adhesive (2 – 8%) compared to the product weight, cost is an issue according to Frihart (2005); and in the context of wood composites, adhesive development is driven by adhesive cost-reduction (Berglund and Rowell 2005). Glued laminated wood construction (glulam) had its beginning at the turn of the 20th century when Otto Karl Hetzer (1846 – 1911) of Weimar, Germany, obtained his first patent for this method of construction. Max Hanisch, Sr. was the first person who brought this new technology to America (Rhude 1996).

The effect of UV light on glulam that is exposed to the sun or other sources of UV light are of great concern to the manufactures of such articles (Renz et al. 2001). Hence, the degradation of glue-laminated beams during weathering has been studied by several scientists. The delamination of glue lines is of particular concern for glulam exposed outdoors. Frangi, Fontana, and Mischler (2004) found out that the shear resistance of gluelam decreased with increasing temperature, when 1-K-polyurethane was used to bond laminae together. Selbo (1965), however, mentioned that melamine formaldehyde glue joints in laminated Douglas-fir beams exposed to the weather showed practically no delamination after about 20 years exposure. Changes of wood moisture content may result in bondline stresses which influence bond-line durability. Phenol resorcinol formaldehyde resin with resorcinol content greater than 16% enhanced the durability and lowered the delamination of CCA treated radiata pine gluelams (Lisperguer and Becker 2005). According to Hofferber et al. (2006) acetylated wood bonded with epoxy adhesives may be expected to show a reduction of the swelling strain and thus the bondline stress, compared to untreated wood. Meierhoefer (1986) demonstrated that waterborne and oil preservatives have a positive effect on moisture change, linear expansion as well as development of checks and delamination of glulam. It is also possible to protect gluelam to some degree against surface checking by using an appropriate coating formulation. Nevertheless, due to the slow diffusion of moisture through the coating, swelling of the wood and thus cracks in the coated surface may still occur. To prevent this phenomena from occurring the surface coating needs to be frequently renewed. It has been found that the diffusion resistance increases linearly with increasing coating thickness. Thus the protection mechanisms of

the coating are assured for a longer period of time when thicker coatings are used (Sell 1983).

Tests have been developed to predict the lifetime of gluelam beams. According to Deppe and Schmidt (1987) the results from short-term tests with glulam may not predict their long term behavior. Hence, they developed an accelerated weathering test for glulam with the aim of predicting the long term behavior of glulam exposed outdoors. The accelerated weathering test involved preliminary exposure of samples in a xenotest weatherometer followed by moisture cycling. Such a test was more effective than moisture cycling alone at reducing glue-bond strength of small glulam specimens (Deppe and Schmitt 1987).

2.8.3. Photocatalytic Effect of Wood on Polymer Degradation

There has been very little research on the photocatalytic effect of wood on polymer degradation. Kiguchi and coworkers (2006) suggested that lignin generated free radicals during photo-irradiation that attacked polypropylene (PP) in wood plastic composites. Polypropylene containing photostabilizers that was artificially weathered for 500 hours didn't show any color changes, which was quite different from that observed for wood plastic composites containing polypropylene. According to Kiguchi et al. (2006) the bleaching of WPC was not only caused by photodegradation of woodfibre, but also by degradation of polypropylene.

Matuana, Kamdem, and Zhang (2001) have done experiments with PVC/wood fiber composites and they concluded that wood fibers are effective sensitizers, and incorporation of wood into a PVC matrix accelerates the photodegradation of the PVC matrix. Their explanation is that the photoinduced breakdown of lignin in wood fibers leads to the formation of chromophoric functional groups such as carbonyls, carboxylic acids, quinones, and hydroperoxy radicals. They suggested that these chromophoric groups accelerate the degradation of polymers in the composite material (Matuana, Kamdem, and Zhang 2001).

2.9. Conclusion

According to Dorn et al. (1992) high humidity and heat have the greatest impact on the strength of adhesives. Osawa (1983) and Searle (2000) both mentioned that UV light is in particular responsible for limiting the lifetime of polymers. Weathering involves complex processes that are still not completely understood for most materials (Searle 2000). Different climatic zones show different magnitudes of each weathering factor, which makes it difficult to develop stable adhesive formulations for all conditions (Jordan 1989). Furthermore, different weathering parameters impact the adhesive usually in combination with each other. Results for individual adhesive types tested under certain weather conditions are not necessarily applicable to other types of adhesives. Therefore, it is recommended to conduct aging tests individual adhesives under different end uses (Dorn and Breuel 1992).

At present the durability of glue lines in wood composites such as glulam exposed outdoors is not of great concern for industry. However with an increasing use of wood-adhesive composites outdoors it will be necessary to increase our understanding of the photodegradation of adhesives used in glulam and the interaction of wood and adhesive degradation.

3. Weathering and Photostability of Adhesives

3.1. Introduction

The history of adhesives is closely related to the history of humans (Keimel 1994). Adhesives surround us both in nature and in our daily lives. The applications of adhesives are numerous as mentioned in the introduction to this thesis. Petrie (2007) concluded that the study of adhesives and the sciences surrounding their application has never been more important.

Adhesives used outdoors are exposed to solar radiation, rain, heat, atmospheric pollutants etc. The combination of these parameters is deleterious to adhesives, and can result in a significant reduction in the performance of bonded products (Dorn and Breuel 1992). Hence, the weathering of adhesives is a major concern (Kockott 1988, Dorn and Breuel 1992, White and Turnbull 1992). Different approaches have been taken to improve the stability of adhesives used outdoors (Horsey 1994, Comyn 1998, Burger 2000). Accelerated aging devices are used routinely to provide predictive and reproducible data on the performance of adhesives in a reasonable amount of time (Horsey 1994). The performance of individual adhesive types tested under specific weather conditions, however, is not necessarily applicable to other adhesive types. Therefore, it is prudent to conduct aging tests for different adhesive types (Dorn and Breuel 1992). In order to understand the resistance of adhesives in wood composites to weathering, which is one of the aims of this study, it is important to evaluate their photostability. This chapter examines the photostability of four clear, light colored, adhesives that may have potential for use in glulam exposed outdoors. This chapter also examines the ability of a selected UVA/HALS stabilizer to protect adhesives exposed to artificial weather conditions. A secondary aim of this chapter was to evaluate the effect of different weathering regimes in two different weatherometers on the degradation of the selected adhesives.

3.2. Materials and Methods

3.2.1. Experimental Design and Statistical Analyses

An experiment was designed to examine the effects of three factors: 1, adhesive type (melamine formaldehyde, epoxide (two types) and, emulsion polymer isocyanate); 2, stabilizer and 3, the interaction of adhesive and photostabilizer on weathering resistance of adhesive films. Loss in weight and tensile strength of adhesive films and changes in color following exposure in two different weathering devices (QUV and Xenon-arc) were used to assess weathering resistance of the different adhesives. Two sets of adhesive samples were prepared and exposed in the different weatherometers.

SEM (Scanning Electron Microscopy) and FTIR (Fourier Transform Infrared) spectroscopy were also used to investigate the effects of weathering on the different adhesives. Results from SEM and FTIR, however, were not subject to statistical analysis.

Analysis of variance was used to examine the effects of adhesive type, stabilizer, and stabilizer/adhesive interaction on factors of interest (tensile strength, weight loss, and changes in color). The results from specimens exposed in the different weatherometers were analysed separately. Computation was performed using Genstat 5 (Genstat 2000). Before the final analysis diagnostic checks were performed to determine whether results conformed to the assumptions of analysis variance, i.e. normality with constant variance. As a result of such checks, tensile strength and weight loss data was converted to natural logarithms before analysis of variance. Significant results are plotted graphically and bars representing the least significant differences are included on graphs to facilitate comparison of means. Appendix 1 contains all data and statistical output.

3.2.2. Sample Preparation

Four different adhesives were assessed (Table 3.1). All of them were nearly colorless because of the market preference for clear glue lines in laminated wood products. Three of them were thermosetting adhesives and the other one, was a thermoplastic adhesive with properties close to thermosetting adhesives (Dynea, n.d.).

Table 3.1: Adhesives assessed for their resistance to weathering

Abbreviation	Full name	Chemical name	Current application
EpE	Epoxy resin and hardener	Butyl glycidyl ether of bispenol-A with polyamide blend	Metal bonding, aircraft industry
EpU	Epoxy resin and hardener	Epoxy resin with glycidyl ether and polyoxy propylene amine type	Metal bonding aircraft industry
MF	Melamine formaldehyde	Methylated melamine formaldehyde polymer and catalyst	Impregnating paper sheets, particleboard, plywood
EPI	Emulsion Polymer Isocyanate	Polyvinyl acetate and dipenylmethane-diisocyanate	Wood glue for environmentally demanding situations, plastic-to-wood

The photostabilizer that was added to adhesive films contained two compounds: (1) Hindered amine light stabilizer (Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate) (trade name: TINUVIN 292); and (2) benzotriazole UV absorber (Iso-octyl-3-(3-(2H-benzotriazol-2-yl)-5-tert. Butyl-4-hydroxyphenyl propionate) (trade name: TINUVIN 384), in a ratio of 1:1 (2% by weight of the adhesive film). Their chemical structures are shown in Figure 3.1.

(1) HALS   (2) UVA
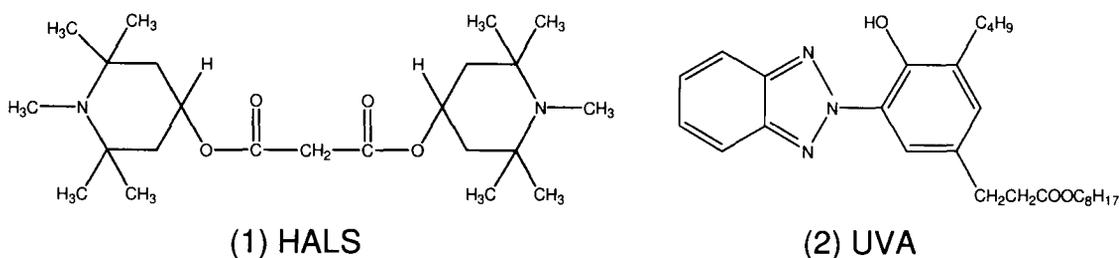
Figure 3.1: Chemical structures of (1) HALS (Tinuvin 292) and (2) UVA (Tinuvin 384)

The different adhesives and hardeners were mixed together in separate polystyrene cups with a total tare weight of ~12 grams for each adhesive. The adhesives were spread out with a paint gauge on a glass surface to form films approximately 450 μm in thickness (Figure 3.2). The two epoxy adhesives were cured at 60 °C in an oven for 150 minutes (EpE) or 180 minutes (EpU). The MF and EPI adhesives were cured under ambient temperatures for 180 minutes. After the adhesive films were cured they were carefully removed from the glass surface with a razor blade (Figure 3.2). Afterwards they were placed on a piece of polyvinylchloride (flooring grade PVC) and 320 samples were punched out from the film strips using a dog-bone shaped cutter (Figure 3.2). One sample per film strip was punched out and allocated to scanning electron microscopy. The samples were labeled on their roughest side (opposite to the one that was adjacent to the glass) using a permanent marker. All samples were placed between plotting paper under weight for three to four weeks in a conditioning room 20 ± 1 °C and at 65 ± 5% relative humidity. The procedure for preparing the dog-bone adhesive samples is shown in Figure 3.2. Before and after the adhesive dog-bone samples were exposed to artificial weathering they were weighed on an AND GR-200 balance, and their color was measured.
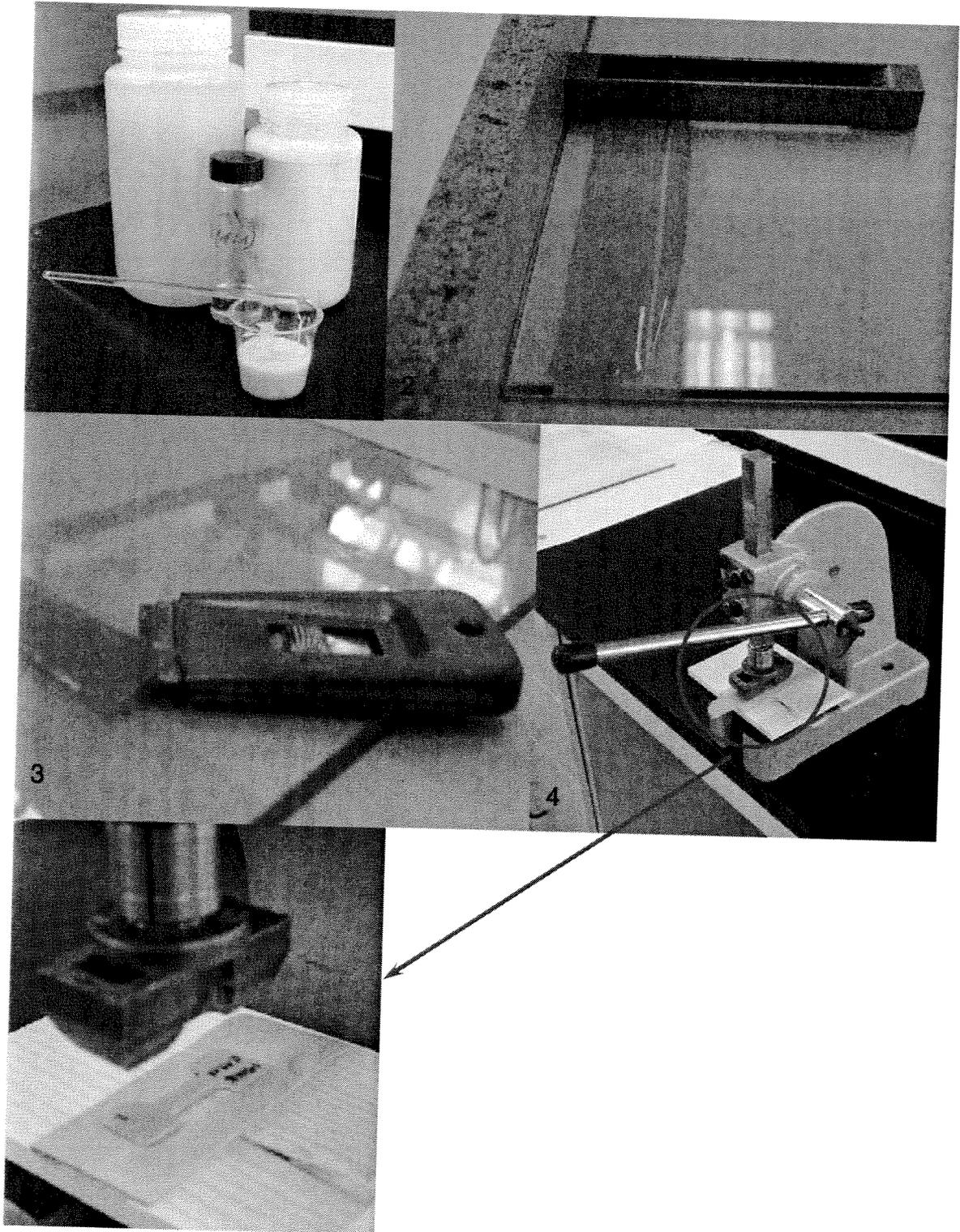
Figure 3.2: Preparation dog-bone adhesive samples; 1, mixing adhesive formulation; 2, spreading out adhesive with a paint gauge; 3, removing adhesive film after cure with a razor blade; 4, samples punched out with a dog-bone shaped cutter; 5, adhesive dog-bone specimen

3.2.3. Colour Measurement

Color measurements were performed using a spectrophotometer (MINOLTA CM 2600d). A total of 505 color measurements were made. Color is expressed using the CIE (Commission Internationale de l'Eclairage) LAB space system, which consists of three parameters; L^* is Lightness (0=black; 100=white), a^* is greenness/redness (-60=green; 60=red), and b^* is blueness/yellowness (-60=blue; 60=yellow). The spectrophotometer was set to SCI (specular component included) and measurements were performed on the side of samples which was exposed to artificial weathering (smoother glass side). Two measurements on the same area of each sample were carried out before and after weathering. The samples were always placed on a yellow plotting paper when their color was measured. Areas of dog-bone specimens that contained voids were avoided when color measurements were made. The total color change deltaE occurring as a result of weathering was calculated according to ASTM D2244 (ASTM 1993). The equation for the calculation of deltaE is (II):

$$(II): DeltaE = ((L_{before} - L_{after})^2 + (a_{before} - a_{after})^2 + (b_{before} - b_{after})^2)^{0.5}$$

3.2.4. Artificial Weathering

Accelerated aging devices are used routinely to provide predictive and reproducible data on the weathering resistance of materials in a reasonable amount of time (Horsey 1994). Laboratory test data from such devices is only applicable to prediction of in-service performance if the mechanism and type of degradation are the same under both types of exposure conditions. The opposing effects of different spectral regions, on the same material shown by the activation spectrum, demonstrates the importance when using accelerated weathering devices of closely simulating natural conditions over the full range of actinic wavelengths. Because the net effect of the radiation source depends on the relative intensities of the short versus long wavelengths, simulation of long wavelength UV and visible radiation can be just as important as simulation of short wavelength UV radiation (Searle 2000). Reliable methods for lifetime prediction of many materials have not yet been developed (White and Turnbull 1992, Kaempf 1984).

In this research, samples were exposed in two different types of weatherometers to increase confidence on conclusions drawn about the weathering resistance of different adhesive/stabilizer combinations. The QUV device is cheaper to buy and hence is commonly used by industry. Xenon-arc when properly filtered closely simulates the full spectrum of the solar radiation. The fluorescent UVA 340 lamps used in QUV devices only match well with daylight in the 300 – 350 nm wavelength region (Searle 2000).

One set of specimens was exposed for 200 hours in a QUV/spray accelerated weathering tester (Q-Panel Lab Products, Cleveland, USA) equipped with fluorescent UVA 340 lamps. The exposure cycle started with a 6 hour conditioning phase at 50 °C to create moisture stress in subsequent cycles. The second step consisted of 8 hours UV light at 70 °C with 0.68 W/m²/nm, followed by 4 hours conditioning at 50 °C. This cycle was repeated 16 times (without the use of water spray).

The other set of samples was exposed in a Xenon-arc weatherometer (Model: 65-W) for 200h. This weatherometer contained a 6500 watt xenon arc lamp with borosilicate inner and outer filters (Atlas Electric Devices, Chicago, USA). The samples were exposed to a slightly different cycle compared to those exposed in the QUV device. This was mainly due to the different technical configurations of the two weatherometers. The main differences between these two weatherometers, besides their different light sources, are that the Xenon-arc device doesn't have a humidifier and its maximum inner temperature is close to 50 °C. In the first step of the Xenon-arc cycle, the samples were exposed to 6 hours of darkness under ambient temperatures. During this stage water spray was used to increase the humidity of the chamber. The second step consisted of 8 hours UV light where the chamber temperature increased to a maximum of 50 °C, followed by 4 hours of darkness with water spray. The water spray was directed onto a shield, which increased the humidity in the chamber and avoided washing the specimens out from their holders. This cycle was repeated 16 times. Figure 3.3 and Figure 3.4 show the QUV and Xenon-arc weatherometers, respectively. In order to remove specimens from their specimen holders after artificial weathering, they were immersed in warm water at about 40 °C for a maximum of 5 minutes.
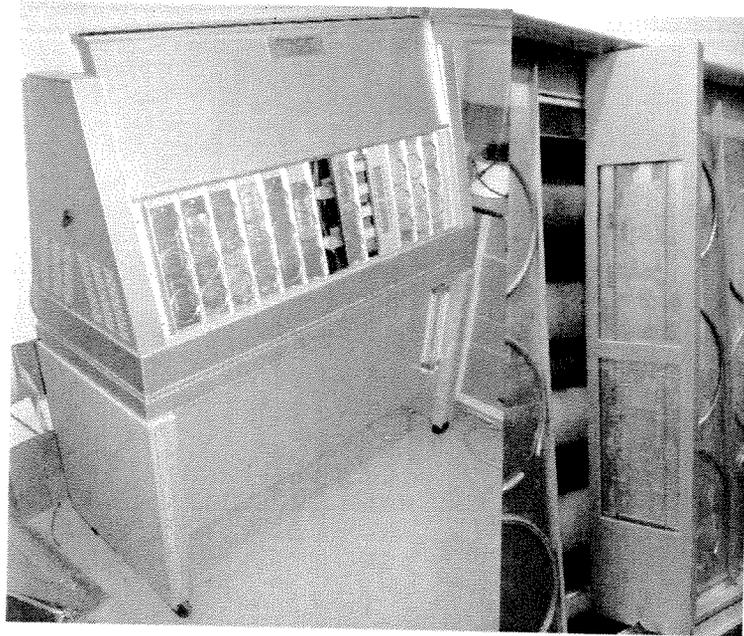
Figure 3.3: QUV weatherometer and dog-bone specimens in sample holder
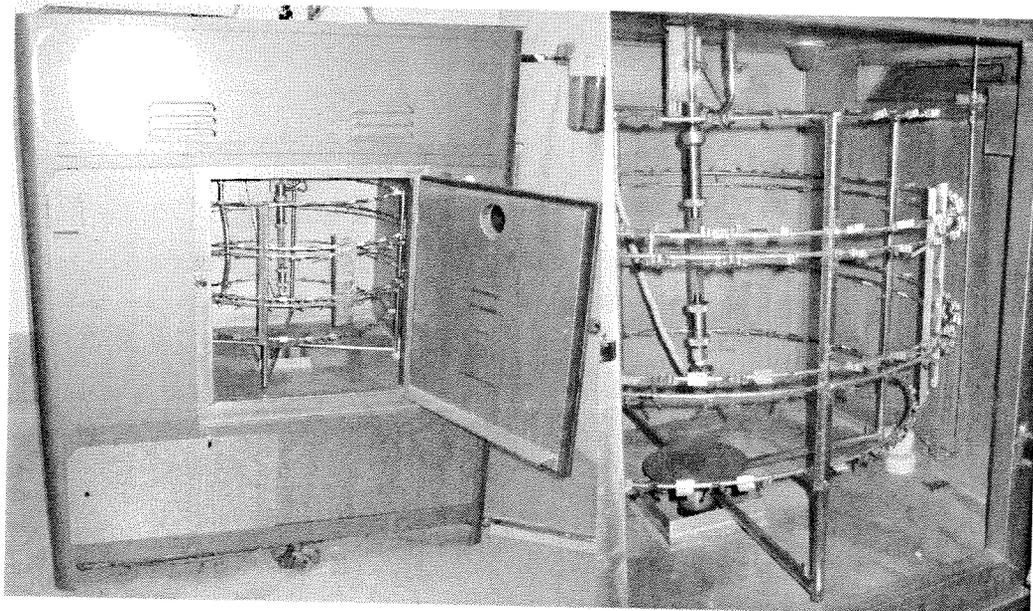
Figure 3.4: Xenon-arc weatherometer and dog-bone specimens in sample holder

3.2.5. Tensile Strength Testing

Tensile strength measures the stress required to pull the adhesive dog-bone samples to a point where they break. Tensile strength forces act perpendicular to the plane of the tested material and, ideally, are distributed uniformly over the cross-sectional area. The fracture will develop where the local stress exceeds the local strength (Petrie 2007). Several studies have shown a relationship, which is not always linear, between loss in tensile strength and increasing exposure time to UV light (Turton and White 2001, Andrady, n.d.).

A QTS 3 Quick Test device from Pruefpartner GmbH (see Figure 3.5) was used to measure the tensile strength of specimens after weathering. Strength tests were also performed on matched, unexposed, controls. Samples were mounted vertically in the jaws of the device and a tensile force was applied to specimens. The testing speed was 20 mm/min, and the maximum testing span of the jaws was 10mm.
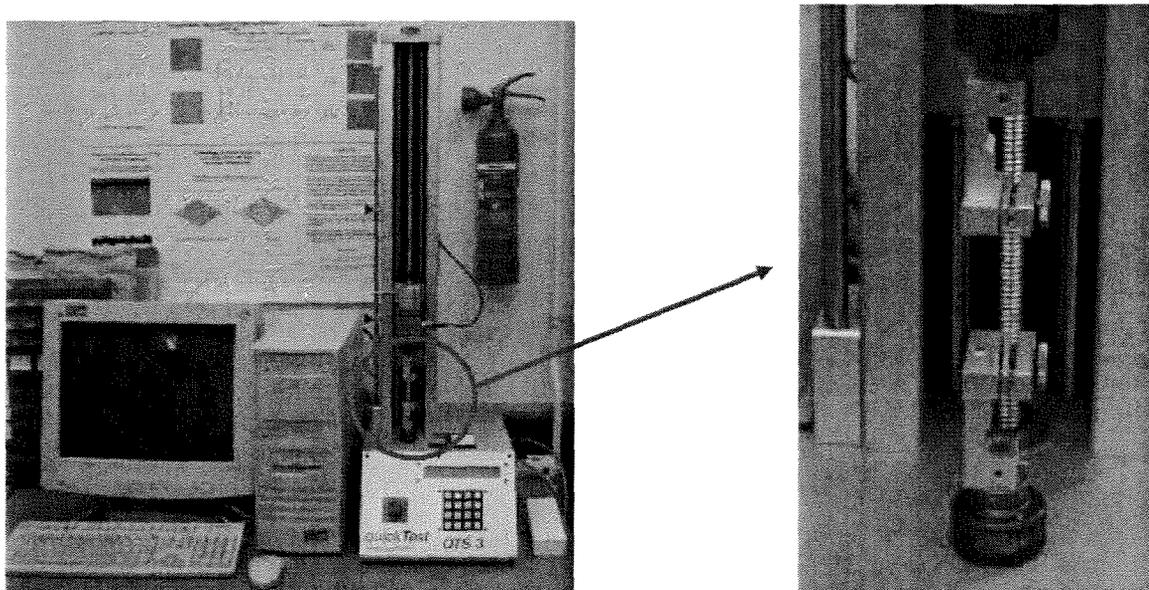
Figure 3.5: QTS 3 Quick test tensile strength tester from Pruefpartner GmbH

3.3 Results

The effects of adhesive type, stabilizer and the interaction of adhesive/stabilizer on tensile strength, weight loss and L* (lightness), b* (yellowness), a* (redness) and delta E (total color change) of specimens after accelerated weathering in the Xenon-arc or QUV weatherometer are summarized in Table 3.2 and Table 3.3.

Table 3.2: Significant effects of and interactions between adhesive type and stabilizer on resistance of adhesive films to accelerated weathering in a Xenon-arc device

Response variable	Experimental factors		
	Adhesive type	Stabilizer	Adhesive/Stabilizer
Tensile strength	***	NS (p = 0.129)	NS (p = 0.537)
Weight change	***	NS (p = 0.731)	NS (p = 0.683)
L* ratio (Lightness)	***	***	***
B* ratio(blue – yellow)	***	***	***
A* ratio (green – red)	NS (p=0.143)	NS (p=0.267)	**
DeltaE	***	***	***

** = p < 0.01; *** = p < 0.001; NS = not significant (p > 0.05)

Table 3.3: Significant effects of and interactions between adhesive type and stabilizer on resistance of adhesive films to accelerated weathering in a QUV device

Response variable	Experimental factors		
	Adhesive type	Stabilizer	Adhesive/Stabilizer
Tensile strength	***	NS (p = 0.300)	NS (p = 0.825)
Weight change	***	NS (p = 0.499)	*
L* ratio (Lightness)	***	NS (p = 0.569)	***
B* ratio(blue – yellow)	***	***	***
A* ratio (green – red)	***	NS (p=0.589)	***
DeltaE	***	***	***

* = p< 0.05; *** = p < 0.001; NS = not significant (p > 0.05)

3.3.1 Tensile Strength

The adhesive type had a significant (p<0.001) effect on the tensile strength of the adhesive films exposed in both types of weatherometers (Table 3.2 and Table 3.3). Figures 3.6 and 3.7 show the tensile strength of glue-film specimens before and after exposure in the Xenon-arc and QUV devices, respectively. The adhesive EpE had the highest tensile strength followed by the melamine formaldehyde specimens. The tensile strength of the EpU epoxy adhesive and the EPI emulsion polymer adhesive specimens were significantly lower. The strength of the different adhesive types was similar in the two different weatherometers (compare Figure 3.6 and Figure 3.7). There were small losses in strength of EPI, EpE and MF specimens exposed in the Xenon-arc weatherometer. Strength losses of these adhesives were more pronounced after exposure in the QUV weatherometer, particularly in the case of the EPI adhesive. In contrast the tensile strength of EPU specimens increased after exposure in the Xenon-arc and QUV devices.
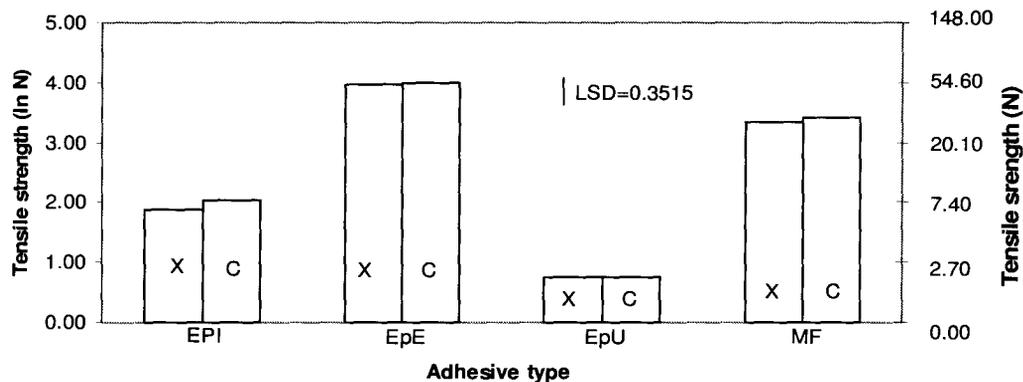
Figure 3.6: Tensile strength of glue-film specimens (X) after exposure in Xenon-arc weatherometer for 200h (results averaged across stabilized specimens and unstabilized controls). Unexposed controls (c) are shown for comparison. Y1 axis shows result on a log scale (natural logarithms, ln) because results were analysed as logs. Y2 axis shows results on a normal scale. The LSD bar is an error bar that can be used to compare means and is used in preference to other types of error bars
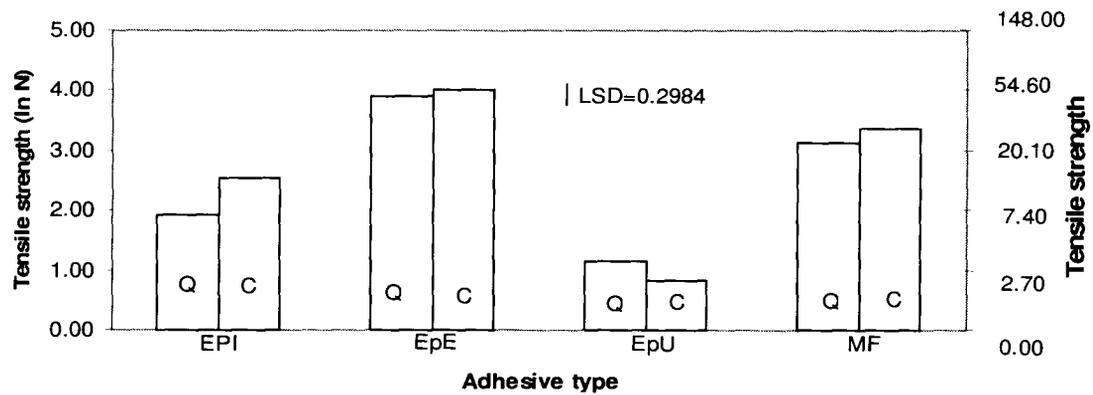
Figure 3.7: Tensile strength of glue-film specimen (Q) after exposure in QUV weatherometer for 200h (results averaged across stabilized specimens and unstabilized controls). Unexposed controls (c) are shown for comparison. Y1 axis shows result on a log scale (natural logarithms, ln) because results were analysed as logs. Y2 axis shows results on a normal scale. The LSD bar is an error bar that can be used to compare means and is used in preference to other types of error bars

3.3.2. Weight Loss

Adhesive type also had a significant (p<0.001) effect on loss of weight of glue-film specimens during accelerated weathering. The weight losses are expressed as ratio of weight of specimens after weathering divided by weight of the same specimen before weathering (Weight$_{ratio}$ = (-weight$_{before}$ + weight$_{after}$)/weight$_{before}$). Figure 3.8 and Figure 3.9 show the weight ratios of glue-film specimens after exposure in the Xenon-arc and QUV devices, respectively.

Weight losses of EpE adhesive films exposed in the Xenon-arc weatherometer were significantly (p<0.05) lower compared to the other three adhesive types. There was no significant difference (p>0.05), between the weight losses of the MF and EpU specimens, but both lost significantly (p<0.05) more weight than the EPI glue film specimens (Figure 3.8).

49
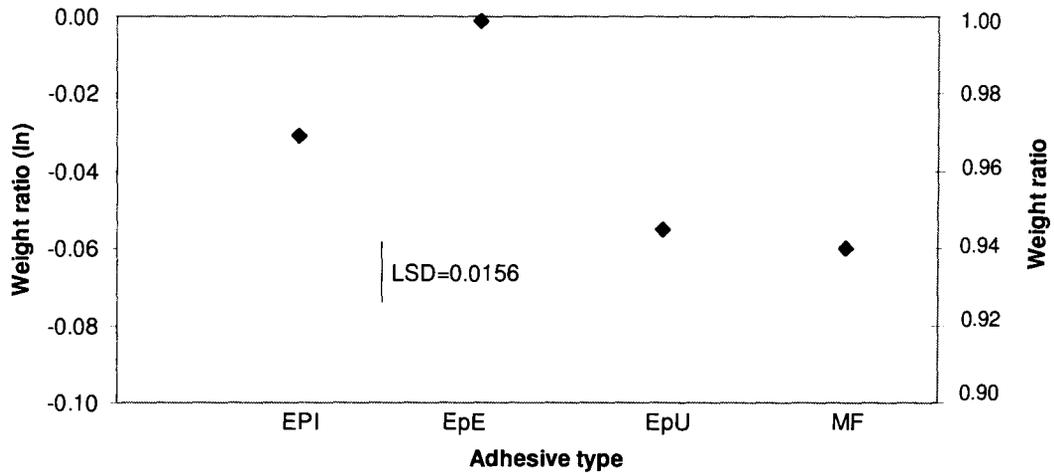
Figure 3.8: Weight losses of glue film specimens after exposure in a Xenon-arc weatherometer for 200h (results averaged across stabilized and unstabilized controls), and expressed as natural logarithms

Weight losses of EpE and EPI adhesive films exposed in the QUV weatherometer were significantly ($p<0.05$) lower than the EpU and MF specimens. There was no significant difference in the respective weight losses of the EpE and EPI films and the EpU and MF films (Figure 3.9).
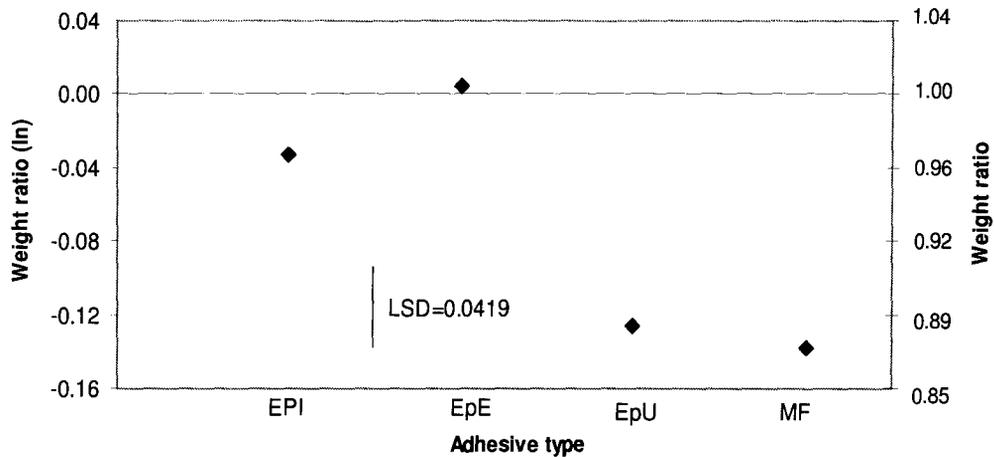
Figure 3.9: Weight losses of glue film specimens after exposure in a QUV weatherometer for 200h (results averaged across stabilized and unstabilized controls) , and expressed as natural logarithms

In general there were similarities in weight losses of samples exposed in the two different types of weatherometers, but MF and EpU samples exposed in the QUV weatherometer lost more weight than those exposed in the Xenon-arc device (compare Figure 3.8 and Figure 3.9).

50

The percentage losses in weight and tensile strength of glue film specimens exposed in both types of weatherometer are summarized in Table 3.4. Positive values represent weight or strength gains.

Table 3.4: Percentage weight and tensile strength losses of glue film specimens exposed for 200h in a Xenon-arc or QUV weatherometer

Weatherometer	Factor	Adhesive type			
		EPI	EpE	EpU	MF
Xenon-arc	Weight loss (%)	3	0.1	5.3	5.8
	Strength loss (%)	13.2	2.4	+9.5	10.6
QUV	Weight loss (%)	3.2	+0.4	11.8	12.8
	Strength loss (%)	44.6	8.6	+77.8	18.4

There was a significant ($p < 0.05$) interaction of adhesive type and stabilizer on the weight losses of specimens exposed in the QUV device (Figure 3.10).
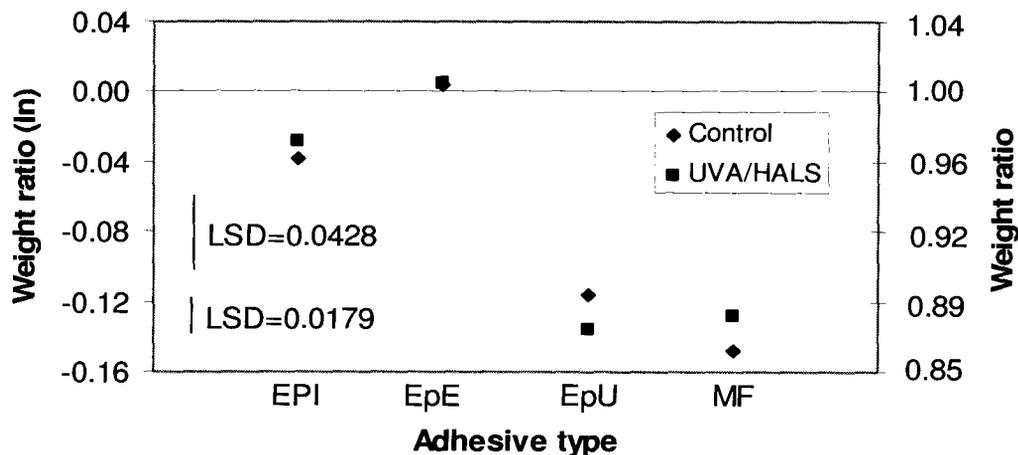
Figure 3.10: Interaction of adhesive type and stabilizer on weight losses of glue film specimens exposed in a QUV device for 200h

The stabilizer had a significant effect at reducing weight loss of MF adhesive dog-bone samples, but the opposite was the case for the EpU adhesive. For EPI and EpE adhesives there was no significant difference in weight losses of the controls and the stabilized glue film specimens. Both the stabilized and unstabilized MF and EpU adhesive samples lost significantly more weight than the EPI and EpE specimens. There were no significant ($p > 0.05$) interactions of adhesive type and stabilizer on tensile strength losses of specimens exposed in the QUV device or weight and tensile strength losses of specimens exposed in the Xenon-arc weatherometer.

3.3.3 Color Change

The colors of the tested adhesives which were visible to the naked eye were: MF = yellow, EPI = light yellow, EpE = grey and EpU = transparent. These colors changed after weathering. Adhesive type had a significant (p<0.001) effect on L* ratio, a* ratio, b* ratio and deltaE of glue film specimens exposed in the QUV. The ratios were calculated by taking the value after weathering and dividing it by the value before exposure. The lightness of the EPI, EpU and MF films decreased significantly when they were exposed in the QUV weatherometer but there was little change in the lightness of the EpE adhesive films. The lightness of all four adhesive types was significantly different from each other. There were significant changes in the redness of EpE, EPI and MF films but not the EpU film. The redness of the EpE film was significantly different from that of the other three adhesive films. There was no significant difference in the redness of the EpU and EPI and the EPI and MF films. The yellowness or b-value of all four adhesive types changed significantly after exposure. There was no significant difference in the b-values of the EPI and EpU films after exposure. The EPI films experienced the greatest color-change, followed by MF, EpU and EpE films. The total color change of all four adhesive types was significantly different from each other. The effect of adhesive type on L* ratio, a* ratio, b* ratio and deltaE of adhesive films after exposure to QUV is shown in Figure 3.11.
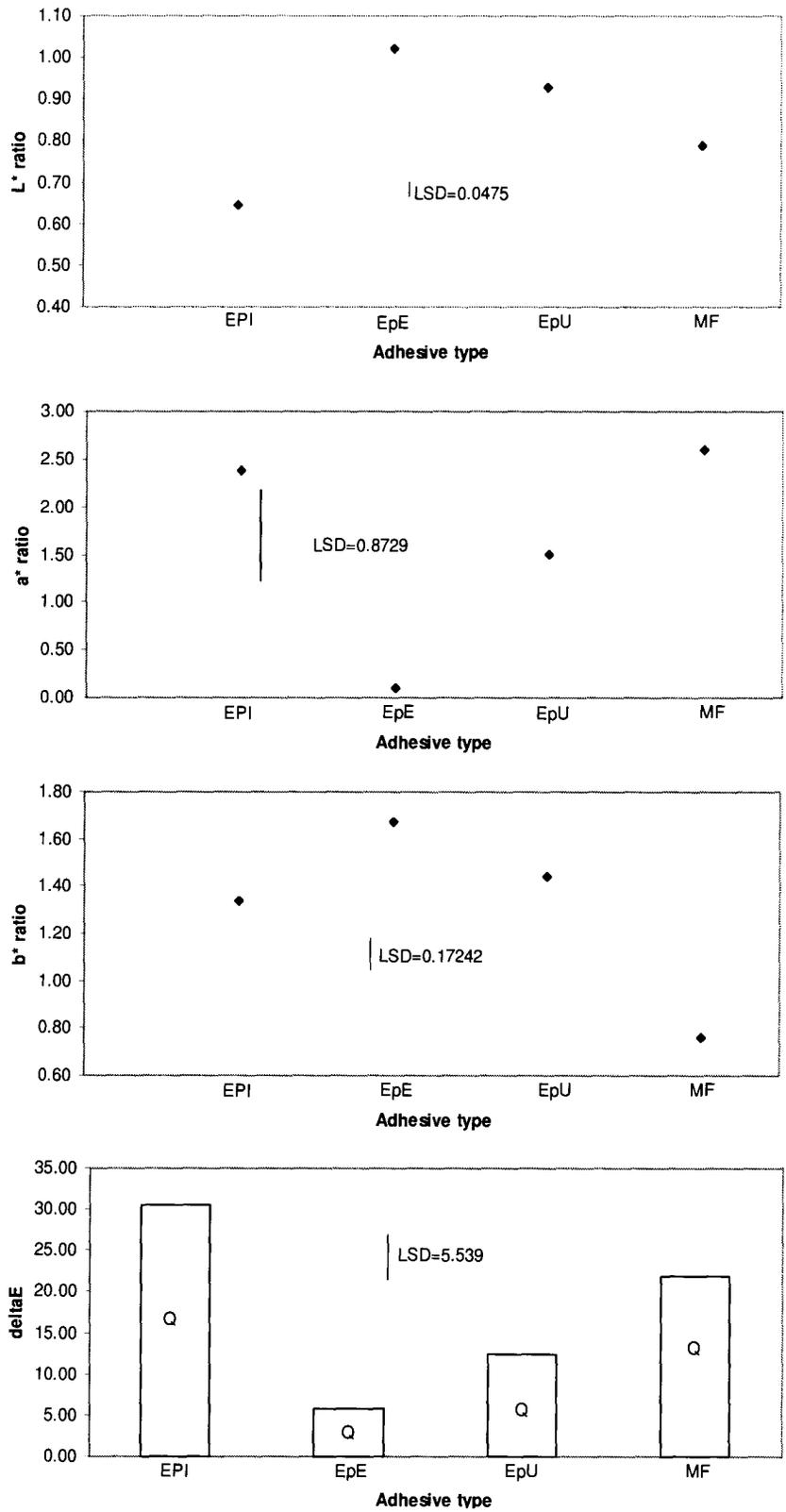
Figure 3.11: Effect of adhesive type on L* ratio, a* ratio, b* ratio and deltaE after exposure to QUV

The stabilizer significantly (p<0.001) reduced the yellowing of the glue films exposed in the QUV device and this is reflected in the lower b* ratio for stabilized films compared to unstabilized ones (Figure 3.12).
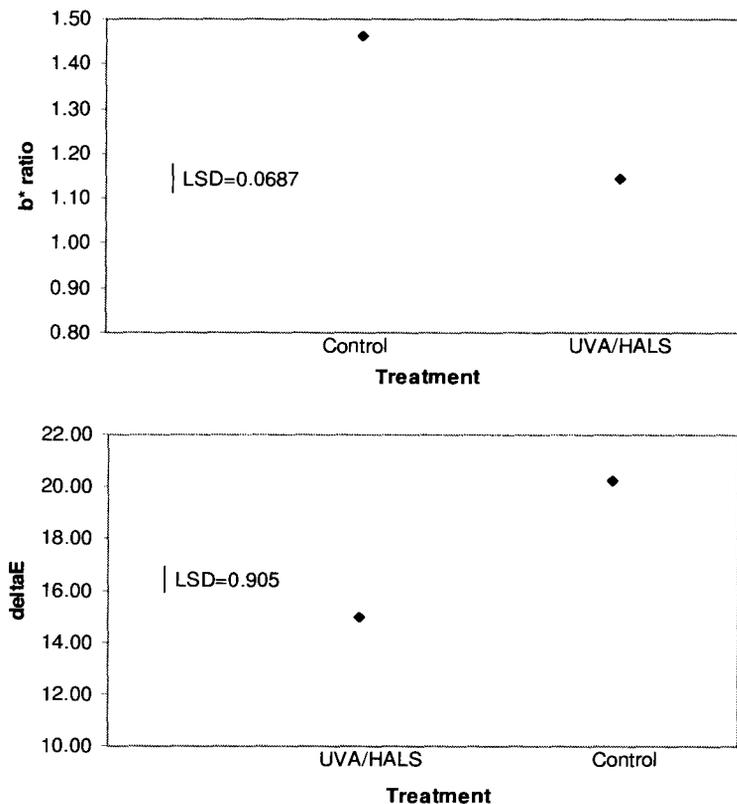
Figure 3.12: Effect of stabilizer on b* ratio and deltaE of glue films after exposure to QUV (averaged across glue types)

There was a significant (p<0.001) interaction of adhesive and stabilizer on L* ratio, a* ratio, b* ratio and deltaE of glue film specimens exposed in the QUV. These interactions occurred because the photostabilizer restricted changes in color of the two epoxy adhesives, but it had little effect in restricting color changes of MF and EPI adhesives (Figure 3.13). The stabilized and unstabilized EPI films showed the largest changes in lightness during exposure followed by MF, EpU and EpE films. The stabilized EpE and EpU showed no significant differences in their L-value during exposure, whereas the other stabilized and unstabilized adhesive films were significantly different. A significant difference in the lightness of stabilized and unstabilized films was only observed for the two epoxide adhesives (EpE, EpU). The stabilized and unstabilized MF and EPI films showed the biggest changes in a* during exposure in the QUV device; followed by unstabilized EpU and EpE films. The redness

54

of the stabilized EpU and stabilized and unstabilized EpE films did not change significantly during exposure. The unstabilized EpE films showed a significant difference in redness compared to the other three unstabilized adhesive films, but EPI, EpU and MF control films were not significantly different from each other. The stabilizer was particularly effective at preventing the reddening of the EpE and EpU (LSD=0.4025, for comparing means with the same level of adhesive) adhesive films, as mentioned above. The stabilizer was also very effective at preventing the yellowing of the epoxy adhesives. In contrast, stabilized EPI films showed slightly greater yellowing than unstabilized specimens and there was little effect of the stabilizer on the yellowing of the MF adhesive films. EPI films showed the greatest total color change during exposure in the QUV device followed by MF, unstabilized EpU, EpE, stabilized EpU and EpE films. The color change of the stabilized EpE and EpU films were significantly different from each other and they exhibited the smallest total color change. The stabilizer was only significantly effective at reducing the total color change in the case of EpE and EpU films.
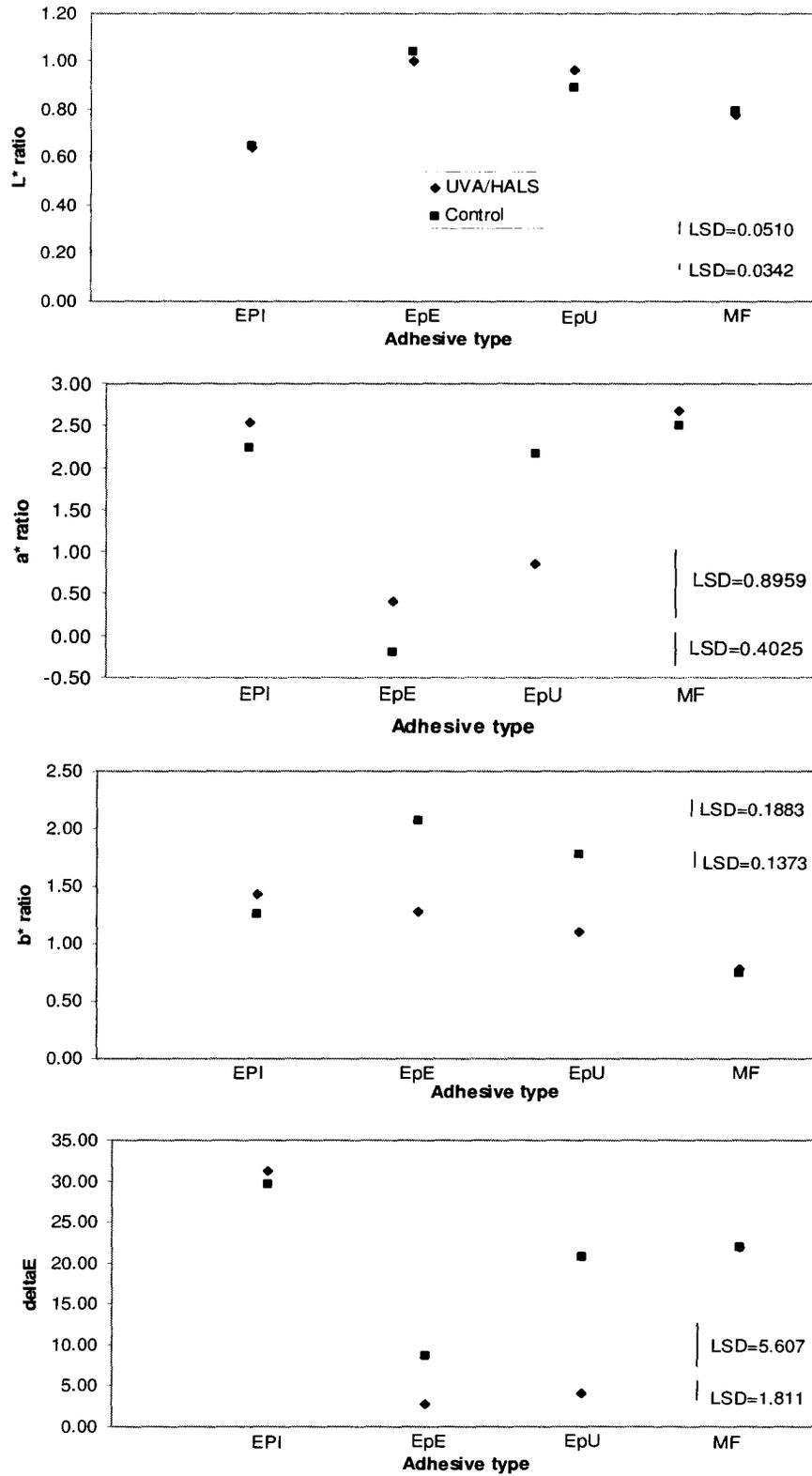
Figure 3.13: Effect of Adhesive/stabilizer on L* ratio, a* ratio, b* ratio and deltaE after exposure to QUV. The smaller numbered LSD is for comparing means of the same adhesive

Adhesive type had a significant (p<0.001) effect on L* ratio, b* ratio and deltaE of glue film specimens exposed in the Xenon-arc weatherometer. The EPI films became darker during exposure in the Xenon-arc device and hence their L ratio was significantly lower than those of the other adhesives. Weathering had no significant effect on the lightness of the epoxy (EpE and EpU) and MF adhesive films and the lightness of these adhesives were not significantly different from each other. All four adhesives became yellow during exposure in the Xenon-arc device and hence there were significant changes in their b-ratios. The EPI showed the greatest total color change, followed by MF, EpU and EpE adhesive films (Figure 3.14). The total color change of the EpE, EpU and MF adhesive films were not significantly different from each other.
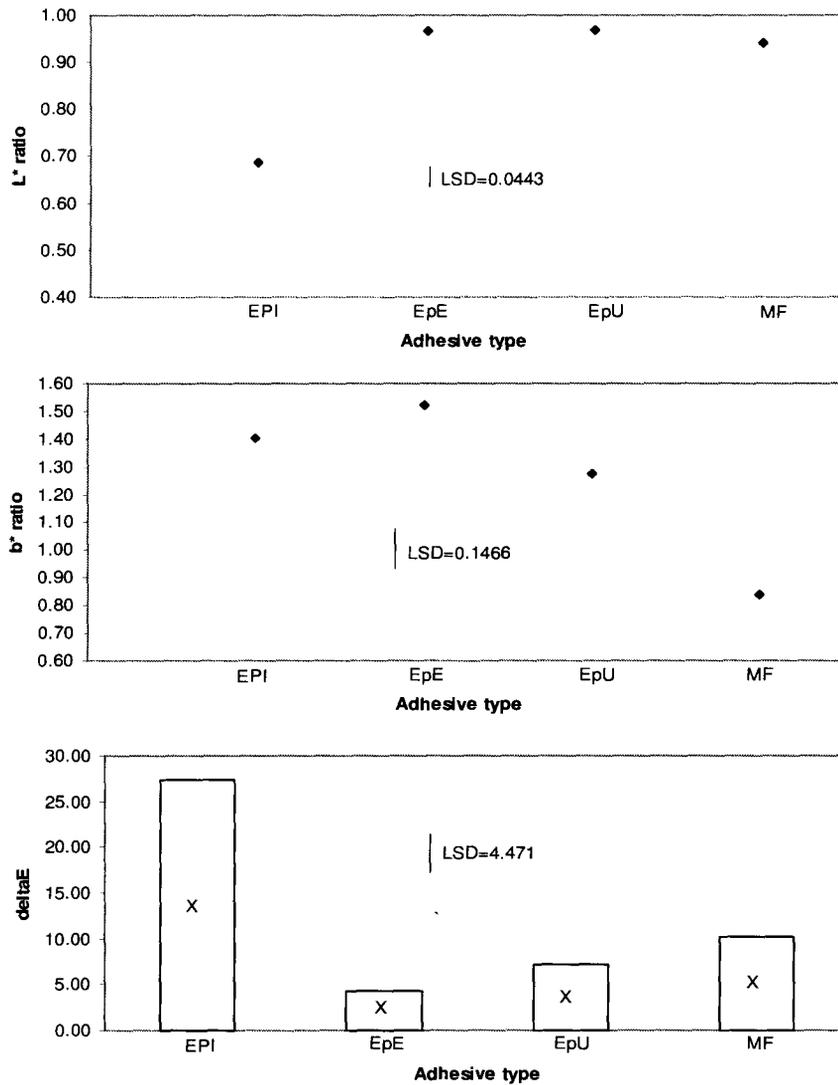
Figure 3.14: Effect of adhesive type on L* ratio, b* ratio and deltaE of adhesive films after exposure in a Xenon-arc weatherometer

Stabilizer had a significant (p<0.001) effect on L* ratio, b* ratio and deltaE of glue film specimens exposed in the Xenon-arc weatherometer. The stabilizer was effective at reducing the darkening (L*) and yellowing (b*) of the glue films during exposure. Accordingly, the total color change (deltaE) of stabilized samples during exposure was significantly smaller than that of unstabilized films. The effect of stabilizer on L* ratio, b* ratio and deltaE after exposure of films in the Xenon-arc weatherometer is shown in Figure 3.15.
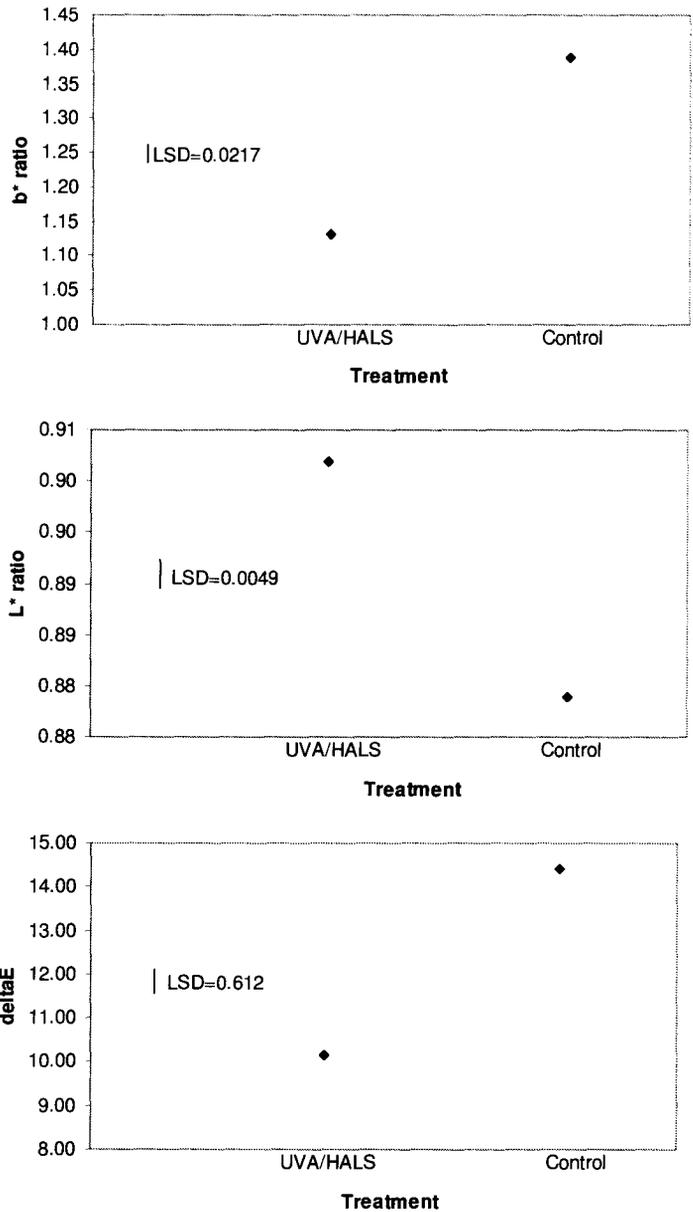
Figure 3.15: Effect of stabilizer on L* ratio, b* ratio and deltaE of adhesive films after exposure in a Xenon-arc weatherometer

There was a significant adhesive/stabilizer (p<0.001) interaction on L* ratio, b* ratio, deltaE and a* ratio (p<0.01) of glue film specimens exposed in the Xenon-arc weatherometer. In terms of lightness the interaction occurred because the stabilizer was effective at reducing the darkening of the EPI, EpE and EpU films, but it was not effective with the MF films. In the case of a-value, the interaction occurred because the stabilizer was effective at reducing the reddening of the EpU films, but it was ineffective at reducing the reddening of the other adhesive types. The interaction of adhesive and stabilizer on the b-value occurred because the stabilizer reduced the yellowing of the

EpE and EpU films but it had no significant effect on the yellowing of the EPI and MF films. The interaction between an adhesive and stabilizer on total color change occurred because the stabilizer was effective at reducing the total color change of EpE and EpU films but it was ineffective at reducing the discoloration of the EPI and MF films. The interactive effect of adhesive type and stabilizer on L* ratio, a* ratio, b* ratio and deltaE after exposure to Xenon-arc is shown in Figure 3.16.
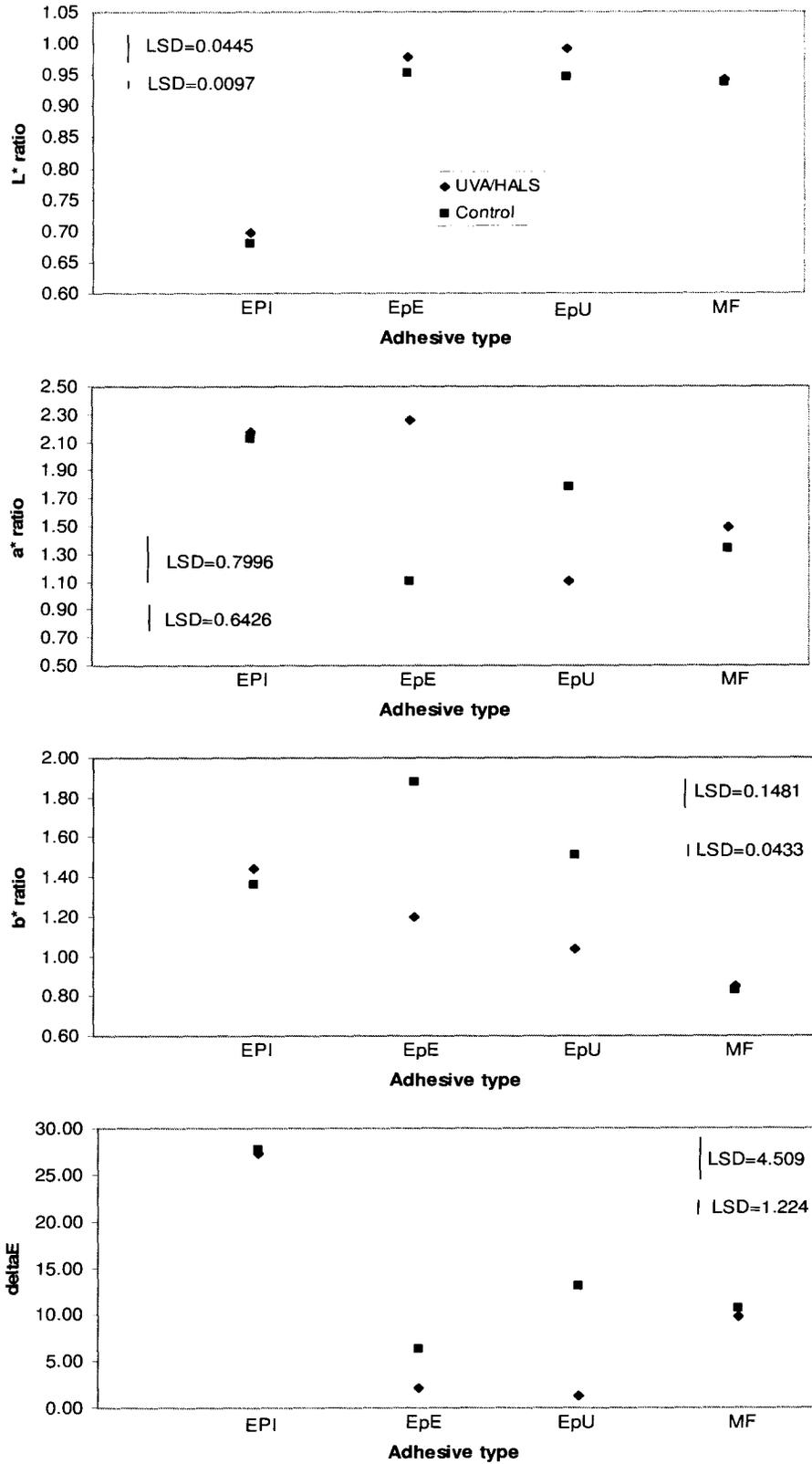
Figure 3.16: Interaction of adhesive type and stabilizer on L* ratio, a* ratio, b* ratio and deltaE of adhesive films after exposure in a Xenon-arc weatherometer. The smaller numbered LSD is for comparing means of the same adhesive

3.3.4 Structural Changes (SEM)

A HITACHI S-2600N Scanning Electron Microscope was used to investigate structural characteristics of different adhesive films before and after weathering. The cross-sections where the dog-bone samples fractured were examined. The prepared samples were coated with a 5 μm thick gold layer after they were glued on a SEM stud. Figure 3.17 – Figure 3.20 show SEM images of unstabilized MF, EpE, EPI and EpU specimens before and after exposure in a QUV weathering device, respectively. Figure 3.21 shows unstabilized MF samples after exposure in QUV and Xenon-arc weathering devices. Figure 3.22 shows unstabilized and stabilized EPI after exposure in a QUV weathering device.
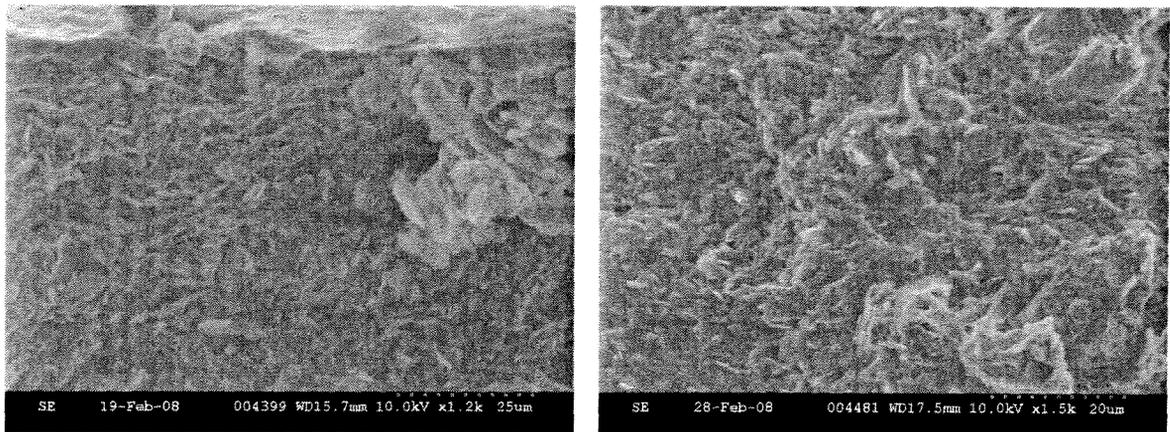
Figure 3.17: Unstabilized MF before (left) and after QUV exposure (right)
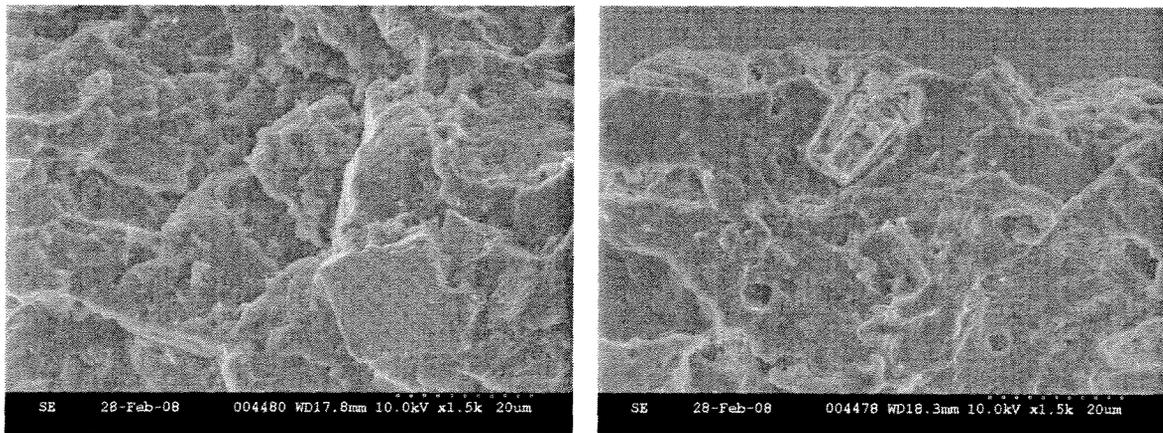
Figure 3.18: Unstabilized EpE before (left) and after QUV exposure (right)
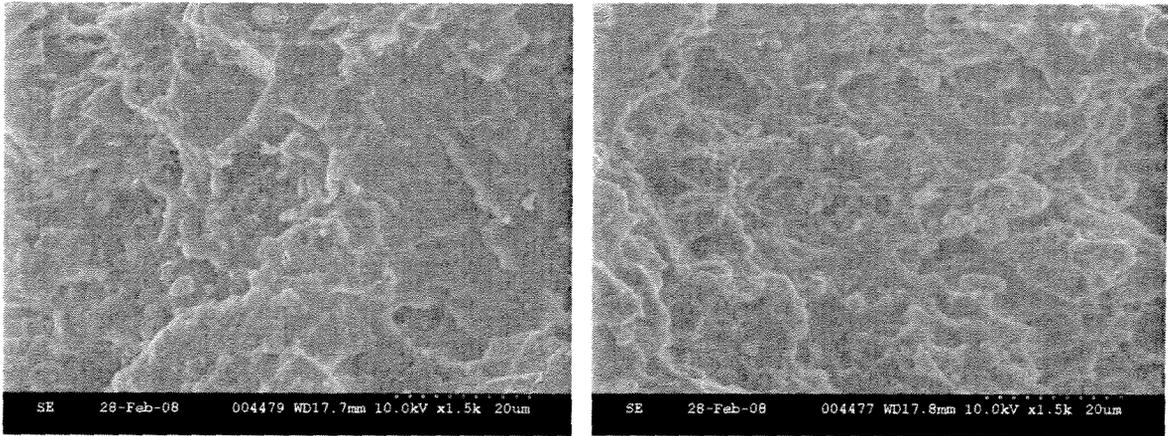
Figure 3.19: Unstabilized EPI before (left) and after QUV exposure (right)
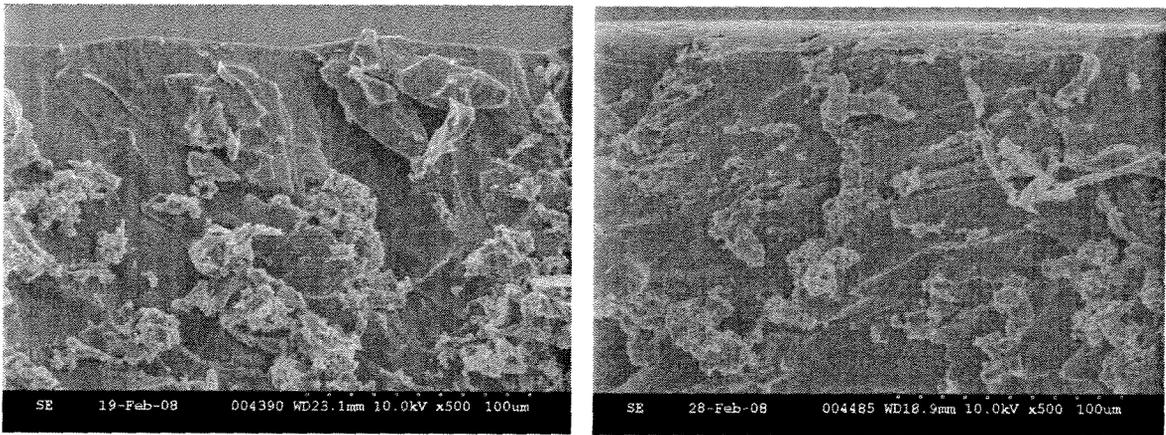
Figure 3.20: Unstabilized EpU before (left) and after QUV exposure (right)
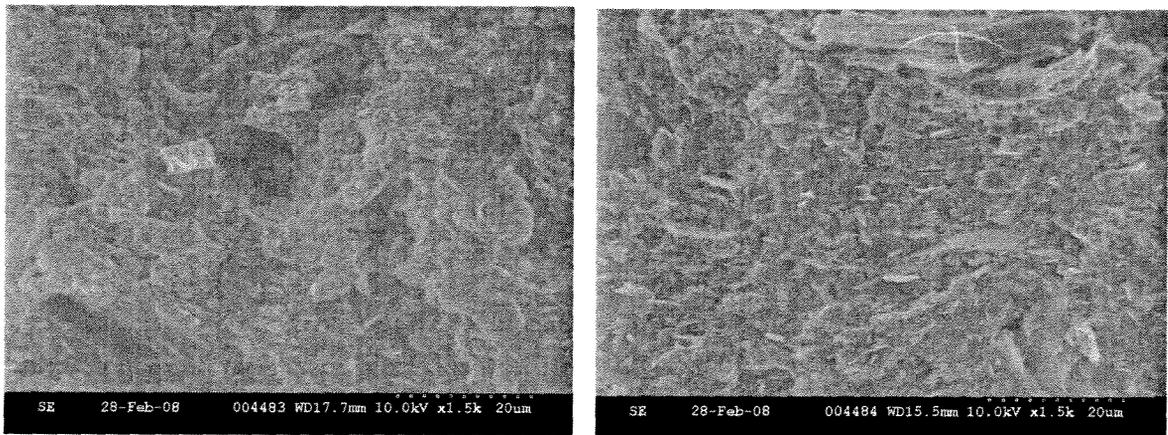
Figure 3.21: Unstabilized MF after QUV (left) and Xenon-arc exposure (right)
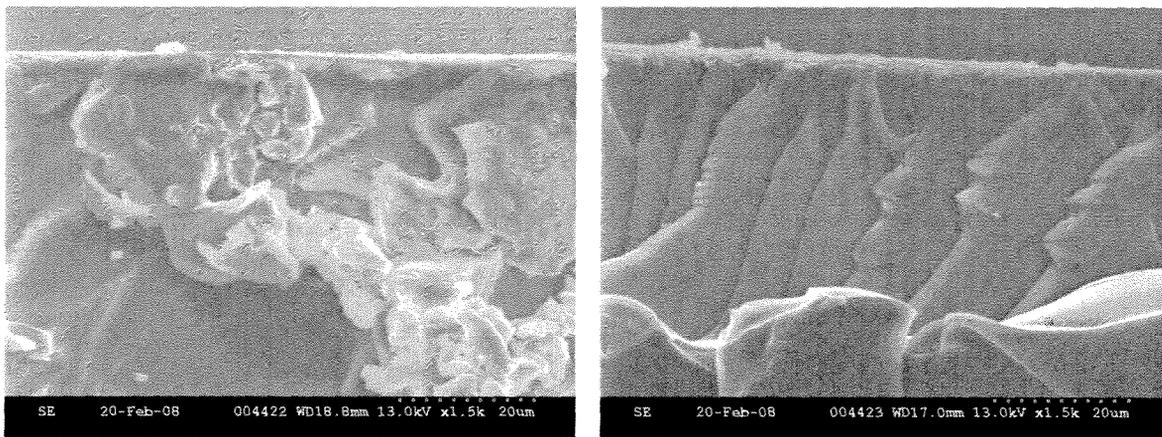
Figure 3.22: Unstabilized (left) and stabilized (right) EpU after QUV exposure

SEM images of adhesive films (Figure 3.17 – Figure 3.22) didn't show any major changes as a result of exposure in the QUV device (Figure 3.17 – Figure 3.20), or between QUV and Xenon-arc exposure (Figure 3.21). Furthermore, there was no difference in the appearance of unstabilized and stabilized films (Figure 3.22). Nonetheless, each adhesive type had a characteristic appearance. The MF appeared to be dense, flaky and rather brittle with some crystalline domains; EpE possessed a compact appearance with larger spots of higher crystallinity. The EPI showed a porous and spongy cross-sectional face and the EpU appeared to be homogeneous over its cross-section. The cloudy patches seen in the EpU image may be an artifact of the way that samples were cut with a razor-blade.

3.3.5 Chemical Changes (FTIR)

The FTIR spectra of adhesive dog-bone samples were taken with a Perkin Elmer Spectrum One FTIR Spectrometer. The resolution was 16 cm^{-1} and 12 scans were performed for each sample and then averaged to produce a spectrum. The following FTIR spectra are given in the range of 650 – 4000 cm^{-1}. Some of the main changes in the functional group of the adhesives were observed in this region.

Figure 3.23 – Figure 3.26 show spectra of unstabilized MF, EpE, EPI and EpU before and after exposure in a QUV device, respectively.
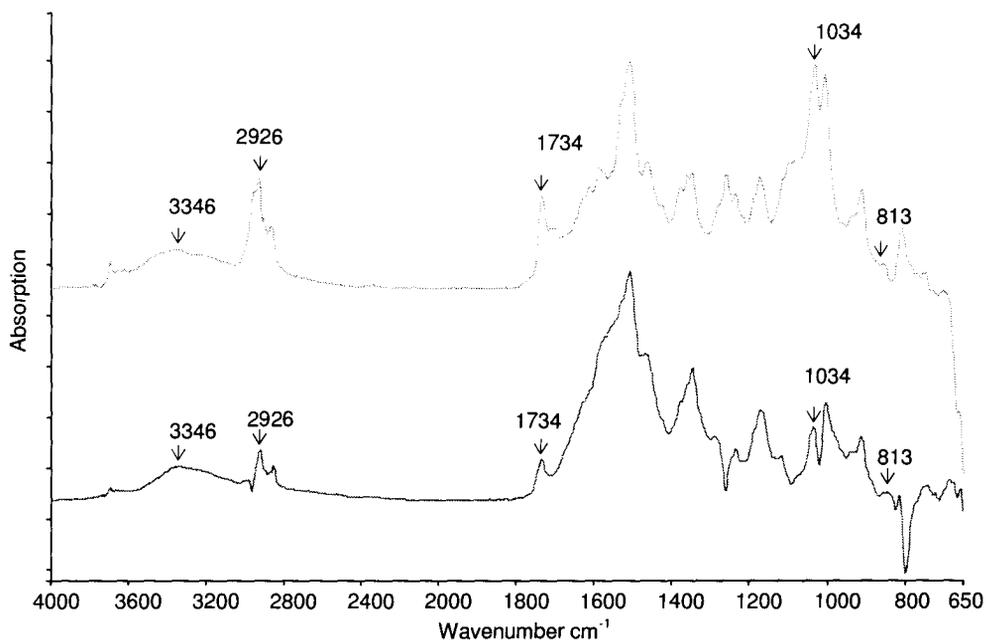
Figure 3.23: Unstabilized MF before (bottom) and after QUV exposure (top)

A slight decrease of the peak at a wavenumber of 1034 cm^{-1} was observed in the MF adhesive after weathering in a QUV device, which may be caused by a loss of ether C-O stretching. Furthermore, a slight increase in the 1737 cm^{-1} band occurred, which may be due to an increase of carbonyl groups. The peak at 2926 cm^{-1} (CH stretching) increased. The peak at 813 cm^{-1} (melamine triazine ring) decreased after accelerated weathering. The band around 3300 cm^{-1} (hydroxyl group) stayed almost constant during exposure (Figure 3.23).
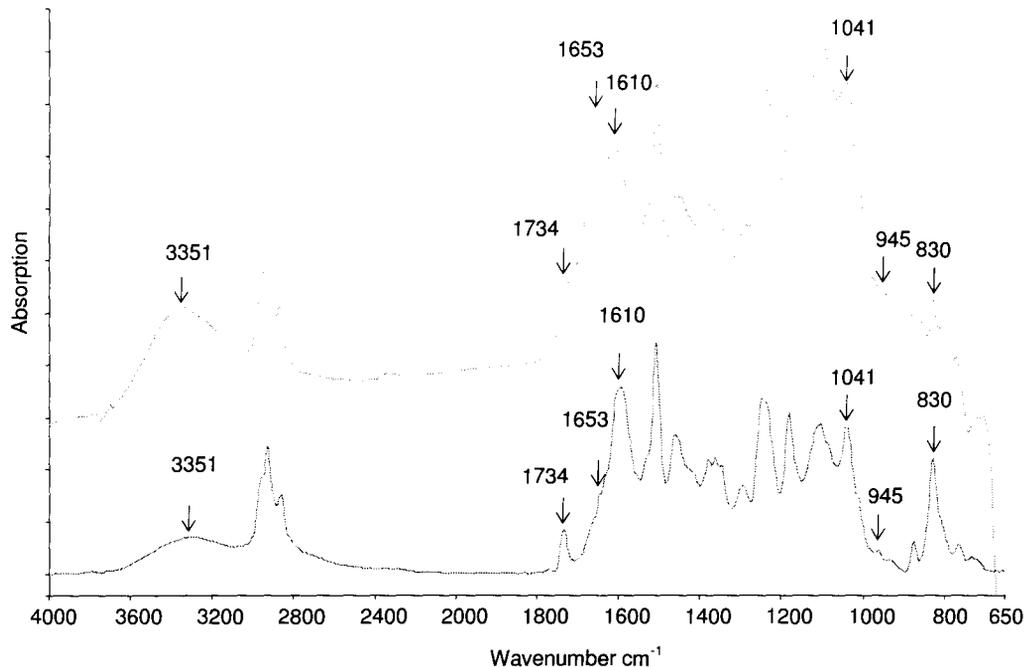
Figure 3.24: Unstabilized EpE before (bottom) and after QUV exposure (top)

The spectra for unstabilized EpE showed an increase in the band at a wavenumber of 3300 cm^{-1} (hydroxyl group) after exposure. The peak at 1734 cm^{-1} (carbonyl group) increased, whereas, a peak at 1653 cm^{-1} (carbonyl group) appeared after exposure. The peaks at 1610 (aromatic C=C), 1041 (C-O group), and 830 cm^{-1} (aromatic CH) also decreased significantly after exposure (Figure 3.24).
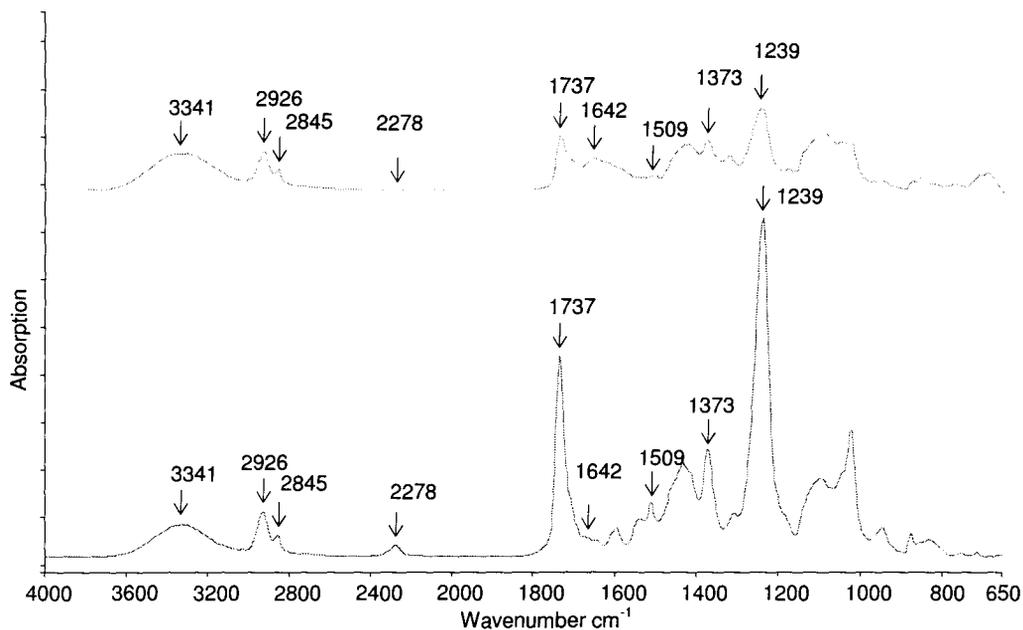
Figure 3.25: Unstabilized EPI before (bottom) and after QUV exposure (top)

In the case of unstabilized EPI the absorption peak at 3300 cm^{-1} (hydroxyl group) stayed constant during exposure in the QUV device. Peaks at 2926 (trans isomer C=C) and 2845 cm^{-1} (trans isomer C=C) decreased slightly after exposure. The peaks at 1737 (carbonyl group), 1373, and 1239 cm^{-1} (amide) decreased significantly and the peaks at 2278 and 1509 cm^{-1} (amide) completely disappeared after exposure. A peak with a wavenumber at 1642 cm^{-1} (carbonyl group) appeared after exposure (Figure 3.25).
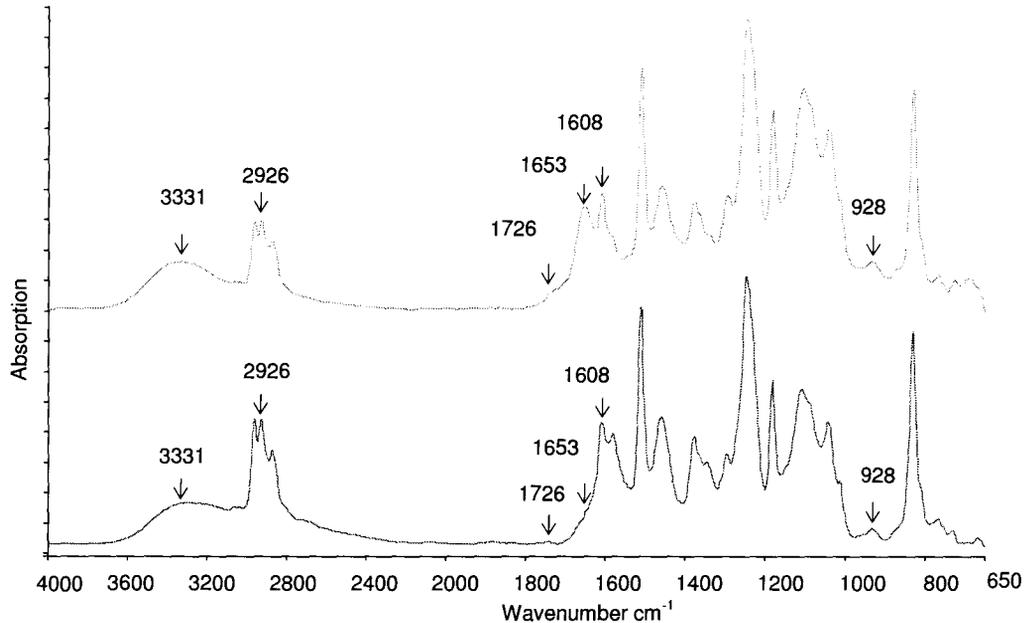
Figure 3.26: Unstabilized EpU before (bottom) and after QUV exposure (top)

The spectra for unstabilized EpU showed a slight increase in the peak at a wavenumber 3300 cm^{-1} (hydroxyl group) after exposure. The peak at 928 cm^{-1} (oxirane ring) decreased slightly. The peak at 1726 cm^{-1} (carbonyl group) slightly increased, and a peak at 1653 cm^{-1} appeared after exposure. The peaks at 1608 (aromatic C=C) and 2926 cm^{-1} (CH$_2$) decreased significantly after the glue films were exposed in the QUV device (Figure 3.26). Both epoxide adhesive types showed different characteristics. The EpE was a grey color and rather brittle and the EpU was clear and very flexible. Nevertheless, the EpU and EpE adhesives have almost the same spectra (compare Figure 3.24 with Figure 3.26), probably because commercial formulations of epoxy adhesives are generally composed of a glycidyl ether epoxy type resin with an amide/amine blend hardener.

Figure 3.27 shows spectra of unstabilized and stabilized EpU films after exposure in the QUV device.
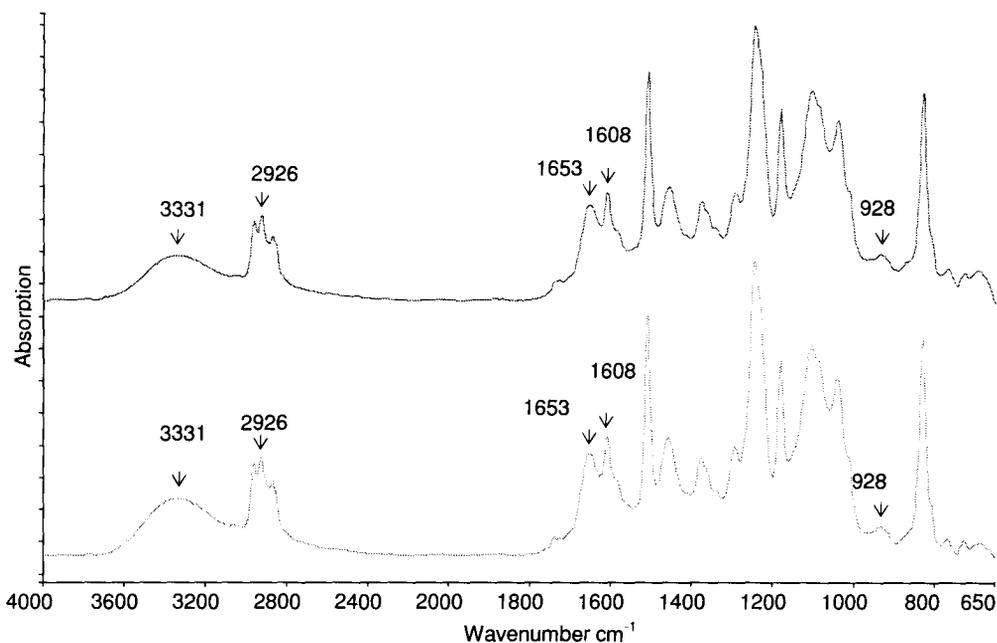
Figure 3.27: Unstabilized (bottom) and stabilized EpU after exposure to QUV (top)

The spectra of the unstabilized EpU after exposure in the QUV device exhibited a higher peak around 3300 cm^{-1}. Peaks at 1653, 1608 and 2926 cm^{-1} are notably higher compared to those in the spectrum of stabilized EPI (Figure 3.27). A peak at 928 cm^{-1} stayed constant.

Figure 3.28 shows spectra of unstabilized MF after exposure to QUV and Xenon-arc
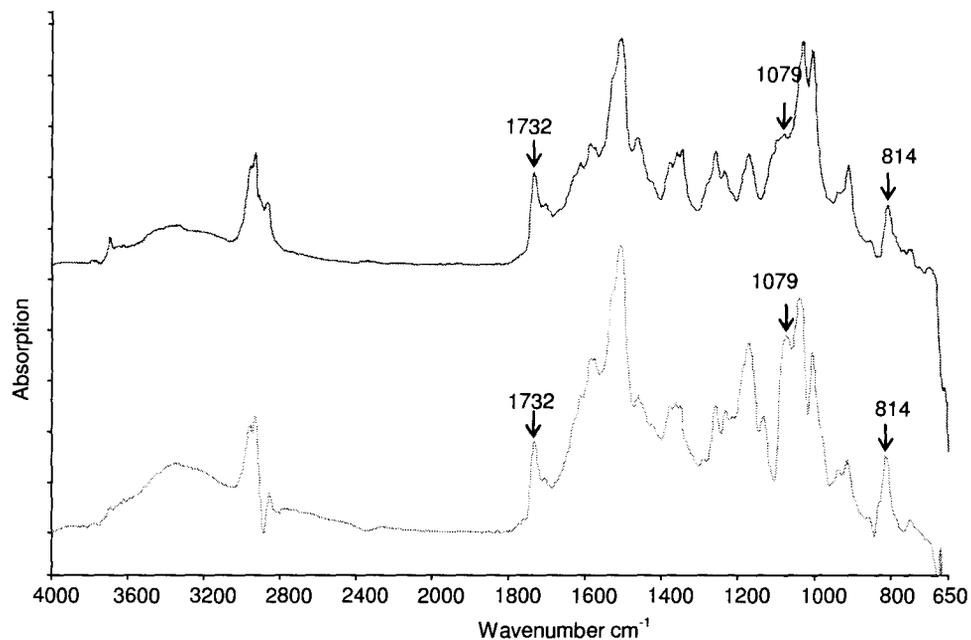
Figure 3.28: Unstabilized MF after exposure to QUV (top) and Xenon-arc (bottom)

The peak at 1732 cm^{-1} has almost the same height after exposure of adhesive films in both types of weathering devices. The peaks at 1079 and 814 cm^{-1} are markedly smaller after exposure in QUV compared to those of samples exposed in the Xenon-arc weatherometer (Figure 3.28).

3.4 Discussion

If the quantum energy present in UV radiation is similar to the dissociation energy of atomic bonds, then bonds can break and a free-radical degradation process may commence (Zeus Industrial Products 2006). Also light absorbing impurities (chromophores) are capable of generating free radical chain scission processes as mentioned in Chapter 2 (Turton and White 2001). Generally, photodegradation can cause reductions in the mechanical properties of polymers (Zeus Industrial Products 2006, Turton and White 2001, Andrady, n.d.). Weathering in the Xenon-arc device, however, did not significantly reduce the tensile strength of the different adhesives. Furthermore, only EPI films lost tensile strength after exposure in the QUV device (Figure 3.5 and Figure 3.6). Some polymers are inherently resistant to UV induced

photodegradation, because of their high bond strength and the absence of UV absorbing structures or impurities (Zeus Industrial Products 2006). The two epoxide adhesives and the MF seemed to have these characteristics. For both epoxy adhesive there were increases in absorption bands at 3300 cm^{-1} (hydroxyl) following weathering and, increases were observed for the EpE adhesive in the peaks at 1724 cm^{-1} and 1734 cm^{-1} (carbonyl). These changes are indicative of photochemical aging of the polymer. As proposed by Ollier-Dureault and Gosse (1998) polymers which photo-chemically age in the presence of oxygen give rise to oxidation products such as alcohols, hydroperoxides, ketones, aldehydes, carboxylic acids, esters, peracids, peroxyesters, and anhydrides. The epoxy adhesive also showed a slight decrease in the ether absorption in the epoxide ring (oxirane ring) around 945 cm^{-1} following weathering. This may indicate that the ring opened up. The major decreases of the characteristic aromatic bands (C=C at 1610 cm^{-1} and CH bands at around 3000 (only EpU) and 830 cm^{-1} (only EpE)) also indicate loss of aromatic groups from the epoxy backbone structure. The ether peak at 1042 cm^{-1} also decreased in the case of the EpE adhesive after weathering. It is assumed that this change resulted from chain cleavages at the oxygen atom. The appearance of ketones and amide stretching at 1660 cm^{-1} for both epoxides are in good agreement with the photo-oxidative mechanism for epoxy cured with aliphatic amines, proposed by Bellenger and Verdu (1983). Ketone formation results from the secondary hydroxyl groups, and amide is generated from the abstraction of hydrogen from methylene groups (CH$_2$) adjacent to the crosslink. Radicals and oxygen are required for both reactions. The appearance of a band near 3300 cm^{-1}, assigned to NH stretching and in the same region as the hydroxyl groups, supports the conclusion of amide formation. As suggested by Rezig et al. (2006) a decrease in the peak at 2925 cm^{-1} (due to CH$_2$ stretching), may be caused by mass loss of the cured material. On the other hand a decrease of both the 1510 cm^{-1} (benzene ring stretching) and 1245 cm^{-1} (aryl-ether stretching) peaks signify chain scission because these bands represent the chemical groups present in the main chains of epoxy resins. This was not observed for both epoxy adhesives. During curing the epoxide ring opens up to produce either alcohol or ether units. Both of these chemical groups are hydrophilic (Comyn et al. 1979) and probably contribute to both the adhesion and water absorption associated with epoxides. Also the slight increase of the 1740 cm^{-1}, 1434 cm^{-1} (EpE) and 1726 cm^{-1} (EpU) stretching bands might be due to the

70

presence of anhydride groups resulting from oxidation according to Le Huy and co workers (1992).

Two of the three thermosetting adhesives (EpE and MF) showed higher tensile strength than the 'thermoplastic' EPI, as expected (Figure 3.6 and Figure 3.5). Thermoset adhesives possess a higher degree of chemical cross-linking, which results in a higher cohesion force between molecular chains. Pure thermoplastics develop no chemical bonds and only secondary bonds that hold the molecular chains together. The former exhibit higher bond energies compared to the latter (Schwarzer 2002). The epoxide adhesive EpU did not break during tensile testing. After force relaxation the sample went back to its original size. This EpU adhesive was initially expected to be a thermoset, but it behaved more like an elastomer, because it exhibited smooth, rubbery-elastic properties. The EpU dog-bone samples were transparent which suggested it had an amorphous structure (Schwarzer 2002). SEM images of EpU cross-sections also indicated its homogenous/amorphous nature (Figure 3.20).

It seems reasonable to assume, that high weight losses of adhesive films during weathering would be associated with losses in tensile strength. In case of EpE this assumption seemed to be correct. The MF adhesive films lost more weight than the EPI films; however, they lost less tensile strength than the EPI films (Table 3.4). It is possible that the MF films weren't completely cured when their weights were taken and loss of water and formaldehyde could account for the relatively high weight losses of the MF films. The higher cross-linking of the MF molecules compared to EPI, may have maintained a stronger structure resulting in less tensile strength losses of MF films during exposure. The emulsion polymer isocyanate consisted of vinyl acetate and an isocyanate type hardener. There is not much information on the FTIR spectra of EPI adhesives, possibly because this adhesive type is relatively new. The band around 3300 cm^{-1} is due to hydroxyl groups and stayed relatively constant or decreased slightly during exposure. The CH stretching bands at 2926 cm^{-1} and 2845 cm^{-1} represent the trans isomer bands of vinyl and these decreased in height after weathering. A small peak at 2278 cm^{-1} was observed before exposure and this completely disappeared after weathering. This band might be due to aliphatic nitriles (RCN) between the vinyl acetate and the isocyanate or due to an aliphatic isonitrile (RNC-), which is at the end of a not completely cross-linked isocyanate where the oxygen atoms dissociate (Nagle et al. 2007). A decrease of the 1740 cm^{-1} band occurred after weathering. According to

Copuroglu and Sen (2004) this decrease is due to ester elimination and the formation of acetic acid. Acetic acid is the main UV degradation product of vinyl acetate. Figure 3.29 shows the evolution of acetic acid from vinyl acetate.

Figure 3.29 has been removed due to copyright restrictions

Figure 3.29: Evolution of acetic acid from vinyl acetate (Copuroglu and Sen 2004)

The formation of aldehydes (1737 cm^{-1}) are thought to be associated with the decrease of the ester peak in vinyl acetate (Copuroglu and Sen 2004). The appearance of the peak at a wavenumber of 1642 cm^{-1} might be due to carboxyl groups (carboxylate ion (RCOO$^-$)). Also the strong increase of the peak at a wavenumber of 1371 cm^{-1} might be due to an increase of carboxylic acid in the polymeric material. In this case the band 1373 cm^{-1} showed a decrease. The amide 2 absorption band (1517 cm^{-1}) and the amide 3 absorption band (1236 cm^{-1}) decreased following exposure of the EPI films in the QUV device. Both stem from isocyanate molecules in the polymeric matrix.

Both natural biopolymer (e.g. wood fiber) and synthetic polymers undergo UV induced discoloration, which is evidence for chemical changes in the polymer matrix (Andrady, n.d., Zeus Industrial Products 2006, Althof 1981). According to Pospisil et al. (2002) there two main contributors to the discoloration of polymers: (a) structural inhomogeneities and impurities absorbing UV-VIS light and (b) products consuming stabilizers which arise from a reaction of stabilizers with alkylperoxy radicals. As mentioned by Clough et al. (1996) the formation of conjugated structures is important in radiation-induced color formation. Generally it was observed, that adhesives with higher tensile strength exhibited less discoloration, as seen in Figure 3.7 and Figure 3.11. EPI was the adhesive which exhibited a significant reduction in tensile strength after QUV exposure, and it also showed the greatest color change (deltaE), compare Figure 3.7 with 3.11. The other adhesives tested here showed far less discoloration than EPI, and little if any changes in tensile strength after exposure. On the other hand, Clough et al. (1996) investigated several polymers including epoxides, and they found that susceptibility to radiation-induced discoloration of polymers had little or no correlation with radiation-induced degradation of their mechanical properties. In support of this

observation Althof (1981) stated that sample discoloration, in itself, may not be related to physical changes in the properties of an adhesive, rather it is more of an indication of modification of the chemical structure of the material. The observations of the behavior of the EpE, EpU and MF film specimens during exposure accord with this statement (compare Figure 3.6 / 3.7 with Figure 3.11 / 3.14). Stark and Matuana (2006) mentioned that cross-linking and chain scission are competitive mechanisms involved in the UV degradation of polymers. Cross-linking has also been shown to be the preferred mechanism during accelerated weathering. Cross-linking and the formation of conjugated structures during accelerated weathering can create colored photodegradation products whereas, mechanical changes would occur due to chain scission. It is possible that cross-linking rather than chain scission reactions predominated in the EpE, EpU and MF specimens and this may account for the observation that discoloration of the adhesives occurred with little loss of mechanical (tensile) properties. Discoloration of EpU due to weathering has been observed previously by Clough et al. (1996). They tested clear amine cured epoxy adhesive and found that they became dark yellow during weathering.

The QUV weatherometer was more destructive towards the adhesive samples than the Xenon-arc weatherometer, as indicated by the weight loss results for the MF and EpU samples (Figure 3.8 and Figure 3.9), and also by FTIR spectroscopy of MF samples before and after weathering (Figure 3.28). The peak at 1732 cm^{-1} (carbonyl groups) for MF samples stayed nearly unchanged after exposure in both types of weatherometers, but peaks at 1079 cm^{-1} (ether C-O stretching) and 814 cm^{-1} (melamine triazine ring) were markedly smaller after exposure in the QUV device, which is consistent with the photo-oxidation mechanism for MF adhesives proposed by Lemaire and Siampiringue (1999). Furthermore, total color change (deltaE) of samples exposed in the QUV was higher compared to samples exposed in the Xenon-arc weatherometer, compare Figure 3.11 and 3.14. The major differences between the weathering cycles used in the two weathering devices are described in detail (above). In brief, however, the QUV exposed samples to light from fluorescent tubes (340 nm) whereas light from the Xenon-arc lamp more closely simulated the characteristics of sunlight. Samples tested in the QUV weatherometer may also have experienced higher humidity and temperatures than those exposed in the Xenon-arc device. The finding that adhesive samples were more degraded in the QUV device than in the Xenon-arc weatherometer

may indicate that short wavelength light and the synergetic effects of heat and moisture are required to accelerate the degradation of adhesives. This observation is in agreement with a statement made by (Searle 2000, Kockott 1988), who mentioned that the synergistic effect of all weather factors is required for decisive degradation of polymeric materials.

Scanning electron microscopy of samples before and after weathering was ineffective at discerning differences between weathered and unweathered samples.

The UVA/HALS stabilizers was only effective at reducing discoloration of the EpE and EpU adhesives (Figure 3.13 and Figure 3.16). The EPI and MF adhesives were the ones which showed the most discoloration, regardless of the addition of a stabilizer. FTIR spectroscopy showed a positive effect of adding stabilizer to EpU (Figure 3.27). Unstabilized EpU adhesive exhibited notably higher peaks at 3300 cm^{-1} (hydroxyl) and 1653 cm^{-1} (carbonyl). A higher peak at 2926 cm^{-1} as shown in the unstabilized spectra is evidence for more complete degradation (above). The effects of the same stabilizer on different adhesive formulations varied and this indicates that different adhesives may require specific and different stabilizer systems to protect them from photodegradation.

Generally changes in the hydroxyl (-OH) (around 3300 cm^{-1}) and carbonyl (C=O) regions (1600 – 1800 cm^{-1}) are evidence for photo-oxidative degradation (Kaczmarek, Podgorski, and Bajer 2005, Nagle et al. 2007). Furthermore, it is mentioned by Kaczmarek, Podgorski, and Bajer (2005) that the presence of carbonyl groups is evidence for impurities in the polymeric material. Samples which were subjected to UV light exhibited yellowing, which is a consequence of the formation of unsaturated groups. These unsaturated groups can be, for example, vinyl, vinylidene, and trans-vinylene groups (Copuroglu and Sen 2004). All four of the adhesives that were tested here are used each for specific purposes, as mentioned above. Based on the results here the EpU adhesive exhibited some promising characteristics, which make it a potential candidate for use in wood composites used outdoors, such as glulam beams. EpU is a clear type of adhesive which showed relatively little discoloration even after 200 hours exposure in the QUV device. This lack of discoloration may be important in composites, where a clear gluline is required. The EpU adhesive also maintained its high flexibility after weathering, whereas often polymers become brittle after exposure (Zeus Industrial Products 2005, Shangguan et al. 2006). A rather flexible adhesive is more capable of accommodating wood swelling and shrinking. The capacity of the EpU

74

to bond wood exposed outdoors and the economics of using this adhesive need to be investigated further.

3.5 Conclusions

The aim of this study was to investigate the performance of four clear adhesives exposed to two different artificial weathering devices, and also examine the potential of a UVA/HALS additive to photostabilize them. The EpE showed the best tensile strength results followed by MF, EPI and EpU adhesive films. The EpE adhesive also exhibited the least discoloration, followed by EpU, MF and EPI adhesive films. The EpE also showed the lowest weight loss. EPI showed the second lowest weight loss followed by MF and EpU. A stabilizer consisting of a UV absorber and hindered amine light stabilizer was effective at reducing weight loss of some of the adhesives and it was effective at reducing discoloration of the adhesives particularly the epoxy adhesives. QUV exposure degraded the MF and EpU adhesives more than Xenon-arc exposure. There was no direct correlation between tensile strength and weight loss. The EpE adhesive showed the best performance overall. Chemical changes still occurred with the EpE adhesive, but they had little impact on its tensile strength and weight loss.

4. Relationship between Wood and Adhesive Photo-degradation

4.1. Introduction

Chapter 3 examined the performance of four clear adhesives under artificial weather conditions. There was evidence of chemical changes and degradation of the four adhesive types. One of the adhesives (EpU) was very resistant to photodegradation. The performance of the MF adhesive was also promising, particularly when a stabilizer was added to it. The experimentation in Chapter 3 focused on the photodegradation of the adhesive alone. The emphasis in this chapter is on the photodegradation of wood and adhesive, as it might occur in a wood composite such as glulam exposed outdoors.

Previous research has not extensively examined the relationship between photo-degradation of wood and adhesives in composites. As mentioned in Chapter 2, a study conducted by Kiguchi and co workers (2006) suggested a relationship between the photodegradation of wood fibre and polymer in wood plastic composites (WPC) (Kiguchi et al. 2006). Matuana, Kamdem, and Zhang (2001) concluded that wood fibers are effective photo-sensitizers and their incorporation into a polymer like PVC accelerates the photodegradation of the polymer when the composite is exposed to UV irradiation. One method of testing whether wood photosensitizes polymers would be to examine changes in the physical (roughness) and chemical properties (discoloration) at the wood-adhesive interface. Materials become rougher when they are exposed to light due to uneven decomposition and loss of molecules/atoms near the exposed surface. Geretovszky et al. (2002) and Wu et al. (2001) both found that mean surface roughness of polymeric films increased almost linearly with irradiation time. Therefore, it seems reasonable to hypothesize that the surface roughness of polymers may be higher in areas where the adhesive photodegradation is accelerated by the photodegradation of wood. Chemical changes which are reflected in discoloration may also be more pronounced at the wood/adhesive interface, for similar reasons.

The aim of this research was to test this hypothesis by examining changes in roughness and color of wood-adhesive samples exposed to natural solar radiation. The results of this experiment are expected to improve the understanding of the relationship

between photodegradation of adhesives in contact with wood, which may lead to the development of wood composites (glulam) with improved durability.

4.2. Materials and Methods

4.2.1. Experimental Design and Statistical Analyses

An experiment was designed to examine the effects of three factors: 1, adhesive type (MF and EpU); 2, stabilizer and 3, the interaction of adhesive and photo-stabilizer on the photodegradation of adhesive dowels in intimate contact with wood. Changes in color and surface roughness of dowels were examined to evaluate the extent of photodegradation of the adhesive.

Analysis of variance was used to analyze the effects of adhesive type, stabilizer, and the interaction of stabilizer/adhesive on factors of interest (changes in color and surface roughness). Computation was performed using Genstat 5 (Genstat 2000). Before the final analysis diagnostic checks were performed to determine whether results conformed to the assumptions of analysis variance, i.e. normality with constant variance. Significant results are plotted graphically and bars representing the least significant difference are included on graphs to facilitate comparison of means. Appendix 2 contains all data and statistical output.

4.2.2. Sample Preparation

Based on results in Chapter 3, two out of the four adhesive types were selected for this experiment. The MF and EpU were chosen because they exhibited reasonable resistance to photodegradation. Furthermore, it was possible to easily cast adhesive dowels from the MF and EpU adhesives whereas the EpE and EPI adhesive were more difficult to cast into dowels. In addition the EpE adhesive was very resistant to photodegradation and it might be difficult to observe the hypothesed phenomenon with such a "photostable" adhesive.

The preparation of adhesives was similar to that described in Chapter 3. The adhesive and adhesive-stabilizer mixtures were placed separately in 20 glass tubes (55 mm in length and with 6 mm inner diameter) with one end of the glass tube closed up

with a paper-stopper. A glass tube was chosen, in order to reduce chemical reactions between the adhesive mixture and the cast. The filled glass tubes were stored vertically for 12 hours at ambient temperature in a rack. Afterwards the glass was removed from the cured adhesive dowel by destroying the glass-tube carefully with light hammer strokes. Then the 20 dowels were cut into half using an ordinary band saw. One half of the original dowel was allocated to UV exposure and the other acted as a control. After labeling the 40 dowels with a permanent marker at their ends, they were stored in a conditioning room at 20 ± 1 °C and 65 ± 5% relative humidity for a period of 7 days.

Wooden samples, 70 (width) x 150 (length) x 15 mm (thickness) were cut from Australian radiata pine boards (*Pinus radiata* D. Don) using an Altendorf table saw. Radiata pine was chosen because it had very wide growth rings, allowing dowels to be inserted exclusively into earlywood. Both Browne and Simonson (1957) and Kataoka, Kiguchi, and Evans (2004) have shown that the penetration depth of light into earlywood is deeper compared to latewood, because of the lower density of earlywood. Deeper penetration of light into wood will presumably enlarge the interface between wood and the adhesive dowel, which should make it easier to distinguish interfacial degradation from that occurring in other parts of the dowel. Before holes were drilled into the wooden samples, the exact diameter of the adhesive dowels was measured using an electronic caliper. According to these measurements an appropriately sized drill bit was selected (5 mm drill bit for MF dowels and 6 mm drill bit for EpU dowels). Four holes of 5 mm depth were drilled into the earlywood of each wooden sample. Two of them with diameters of 5 mm were allocated at random to the MF dowels and the other two, which had diameters of 6 mm were used for the EpU dowels. The holes were drilled using an ordinary manual drill press. Prior to exposure, the dowels were inserted tightly into the holes so that they protruded at least 5 mm above the surface of the boards. Figure 4.1 shows a sample board containing a dowel. Three regions can be identified within each dowel; (1) Region 1 is fully exposed to sunlight; (2) Region 2 is the interface between wood and adhesive where sunlight acts on both wood and adhesive; (3) Region 3 is a zone where sunlight does not act on the wood and adhesive. Five wood-adhesive-dowel samples were exposed to solar radiation, and the remaining 5 samples were stored in a conditioning room.

1. UV + O_2
2. UV + O_2 + Wood
3. O_2 + Wood

UV
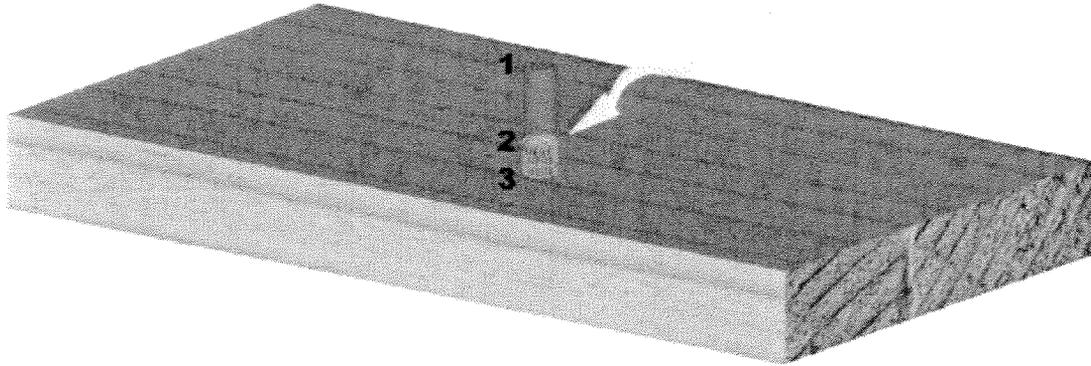
Figure 4.1: Sample board showing a dowel and interfaces between the dowel, wood and the atmosphere

The experimental sample was designed to create a good interface between the wood and adhesive dowel. An interface is described [according to ASTM Standard D 907-00, ASTM International 2001] as "a region of finite dimension extending from a point in the adherend where the local properties (chemical, physical, mechanical and morphological) begin to change from the bulk properties of the adherend to a point in the adhesive where the local properties are equal to the bulk properties of the adhesive". The bulk properties are the properties of one phase unaltered by the other phase. The interfacial region has different chemical and physical attributes compared to the bulk material (adhesive or adherend). Therefore, the interface properties critically influence the properties of the adhesive bond (Petrie 2007). The least clear failure zone according to (Frihart 2005) is that occurring within the interface. An important requirement in order to observe the hypothesed phenomenon (above) is a tight fit between the adhesive dowels and the wooden samples. As mentioned by Frihart (2005), in order for an adhesive to chemically bond to a substrate, intimate contact between both components is required. Region 2, which is the interfacial zone, was only examined using profileometry. This zone was too narrow to measure its color using a spectrophotometer.

4.2.3. Natural Weathering

The wood-adhesive-dowel samples were exposed to 195 sunshine hours at the Center of Advanced Wood Processing in Vancouver/Canada from the first of July 2007 to the 15th of September 2007 (Table 4.1). The samples were not exposed to any rain.

Table 4.1: Dates when adhesive dowels were exposed to sunlight, and total sunshine hours and mean temperature during the exposure trial

Date	Sunshine hours	Mean temperature [C]
2007-07-31	6.5	17.4
2007-08-01	6.5	18.9
2007-08-02	6.5	20.4
2007-08-03	6.5	18.6
2007-08-04	6.5	17.4
2007-08-05	6.5	18.6
2007-08-06	6.5	18.1
2007-08-07	6.5	16.7
2007-08-13	6.5	16.8
2007-08-14	6.5	17.8
2007-08-15	6.5	19.1
2007-08-16	6.5	18.4
2007-08-24	6.5	19.4
2007-08-25	6.5	17.1
2007-08-29	6.5	19.4
2007-08-30	6.5	20.4
2007-08-31	6.5	17
2007-09-01	6.5	15.3
2007-09-02	6.5	15.8
2007-09-05	6.5	16.9
2007-09-06	6.5	15.8
2007-09-07	6.5	14.9
2007-09-08	6.5	14.4
2007-09-09	6.5	16.8
2007-09-10	6.5	16.9
2007-09-11	6.5	17.4
2007-09-12	6.5	16.2
2007-09-13	6.5	15.4
2007-09-14	6.5	16.6
2007-09-15	6.5	15
Total	195	Average 17.3

4.2.4. Roughness Measurement

An AltiSurf 500 profilometer was used to scan the adhesive-dowel surface in order to obtain mean roughness values (Sa), which were analysed statistically, and also to visualize the surface profile at the interface between wood and adhesive that was exposed to sunlight. A 9 mm^2 surface was scanned across the three regions of the dowels (1 through to 3). A 300 μm probe was used to scan samples and measure their surface roughness. Measurement of surface roughness was performed before and after exposure of dowels to sunlight. The samples were placed on a sample-holder in a way that ensured that the same surface was scanned before and after exposure. The average roughness (Sa) was obtained for each region within the dowel, and the software (Paper Map version 3.2.0) was used to create topographical maps of the areas that were scanned.

4.2.5. Colour Measurement

A Minolta spectrophotometer was used to measure the color of samples both before and after exposure. Each sample was measured twice. Once in region 3 which was surrounded by wood and once at the top of the dowel that was directly exposed to natural sunlight (region 1). The total color change deltaE occurring as a result of exposure was calculated as described in Chapter 3. The ratio of color before and after exposure was calculated and analysed statistically.

4.3. Results

There were significant effects of adhesive type, stabilizer and interactions of adhesive/stabilizer on L* ratio (lightness), b* ratio (yellowness), a* ratio (redness), deltaE and Sa ratio (roughness) of adhesive-wood samples after exposure to solar radiation which are summarized in Table 4.2.

Table 4.2: Significant effects of and interactions between adhesive type and stabilizer on resistance of adhesive dowels to solar radiation

Response variable	Experimental factors		
	Adhesive type	Stabilizer	Adhesive/Stabilizer
Sa ratio (roughness)	NS (p = 0.348)	*	NS (p = 0.889)
	Exposed part of dowel (region 1)		
L* ratio (Lightness)	NS (p = 0.120)	NS (p = 0.777)	*
b* ratio(blue – yellow)	***	NS (p=0.795)	NS (p=0.305)
a* ratio (green – red)	*	NS (p=0.071)	**
DeltaE	NS (p=0.334)	NS (p=0.101)	*
	Unexposed part of dowel (region 3)		
L* ratio (Lightness)	NS (p=0.178)	NS (p = 0.773)	NS (p=0.829)
B* ratio(blue – yellow)	NS (p=0.286)	NS (p=0.599)	NS (p=0.277)
A* ratio (green – red)	**	NS (p=0.094	NS (p=0.061)
DeltaE	NS (p=0.249)	NS (p=0.515)	NS (p=0.502)

* = p < 0.05; ** = p < 0.01; *** = p < 0.001; NS = not significant (p > 0.05)

4.3.1 Roughness Changes

Adhesive type had no significant (p>0.05) effect on the roughness of adhesive dowels that were fully exposed to solar radiation, and there was no significant (p>0.05) interaction of adhesive and stabilizer on surface roughness. The stabilizer, however, had a significant (p<0.05) effect on the surface roughness of adhesive dowels exposed to solar radiation (Table 4.2). Figure 4.2 shows the roughness ratio of stabilized and unstabilized dowel samples after exposure. The unstabilized dowels were rougher than the stabilized ones after exposure, as expected.
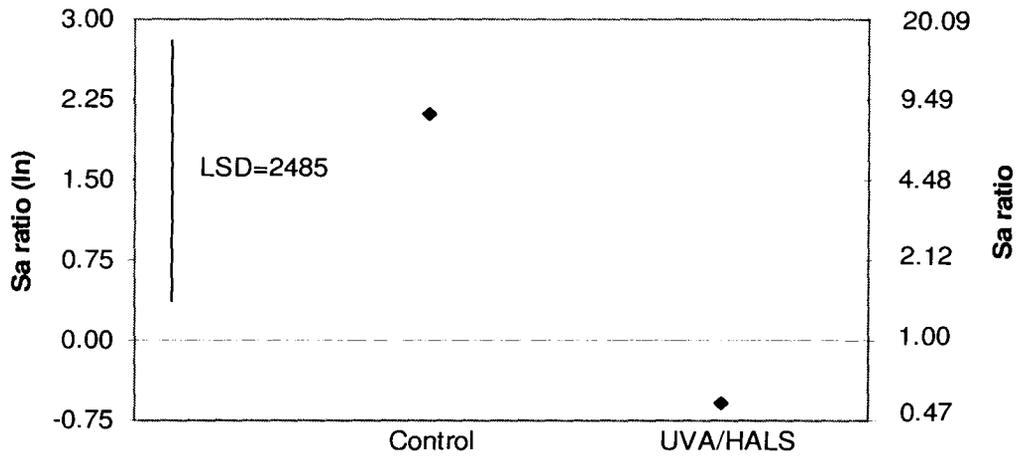
Figure 4.2: Effect of stabilizer on surface roughness ratio of adhesive dowels after exposure to sunlight, and expressed as natural logarithms

4.3.2 Color Changes

Adhesive type had significant effects on the b* and a* ratio of the part of the dowels that were fully exposed to solar radiation, and the a* ratio of the part of the dowel that was exposed to light and wood. There were also significant interactions between adhesive and stabilizer on L*, a* and deltaE of dowel sections that were fully exposed to solar radiation. There were no significant ($p>0.05$) effects of stabilizer on any of the color parameters. The effect of adhesive type on b* ratio and a* ratio of dowel sections that were fully exposed to solar radiation is shown in

Figure 4.3. The exposed part of the EpU dowel showed significantly less yellowing than the exposed part of MF dowels, but the opposite was the case for a*, in which case the MF was significantly less prone to redening than EpU adhesive.
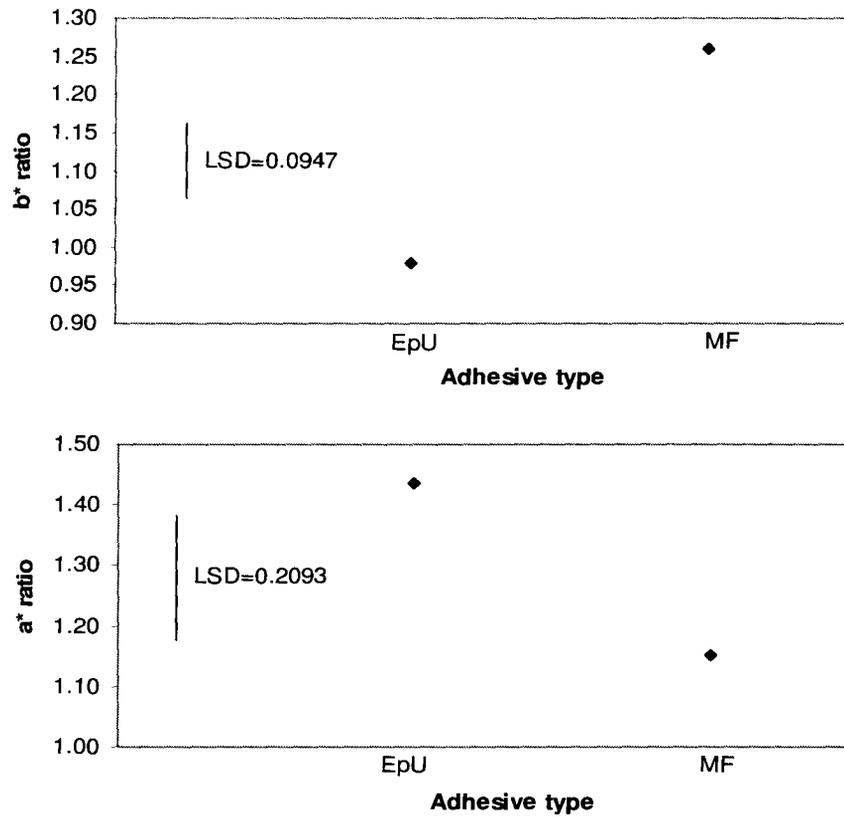
Figure 4.3: Effect of adhesive type on b* ratio and a* ratio after full exposure of dowels to solar radiation

The effect of adhesive type on a* ratio of dowels after exposure to solar radiation and wood (region 1) is shown in Figure 4.4. Adhesive type also had a significant (p<0.01) effect on the a* ratio of that part of the glue dowel samples which was surrounded by wood (region 3). The unexposed part of the MF dowel showed significantly less redening than the unexposed part of EpU dowels.
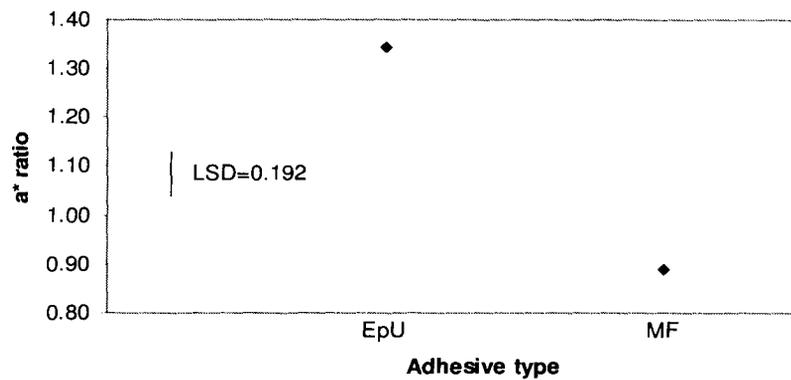
Figure 4.4: Effect of adhesive type on a* ratio after exposure to solar radiation (region3)

There was a significant interaction between adhesive and stabilizer on lightness. Unstabilized MF which was fully exposed to solar radiation showed a smaller change in lightness than unstabilized EpU. Stabilized and unstabilized EpU samples, which were fully exposed to solar radiation were not significantly (LSD=0.0498, for comparing means with the same level of adhesive) different from each other, in terms of their lightness (Figure 4.5). The same trend was observed for fully exposed MF samples. Table 4.3 shows the lightness values of fully exposed unstabilized and stabilized EpU and MF samples.

Table 4.3: Lightness/color values of fully exposed unstabilized and stabilized MF and EpU samples

	Control	UVA/HALS
EpU	0.9617	0.9956
MF	1.0297	0.9868

There was also a significant interaction between adhesive and stabilizer on the a* ratio of samples because the stabilizer restricted the redening of EpU dowels that were fully exposed to solar radiation, but the opposite was the case for the MF specimens. Also unstabilized EpU exhibited significantly ($p<0.05$) more redening than unstabilized, fully exposed MF dowels. As for deltaE, there was a significant ($p<0.05$) interaction between adhesive and stabilizer because the stabilizer restricted discoloration of EpU dowels that were fully exposed to solar radiation, but the opposite was observed for MF specimens. The interactions between adhesive and stabilizer on L* ratio, a* ratio and deltaE after full exposure of dowels to solar radiation are shown in Figure 4.5.
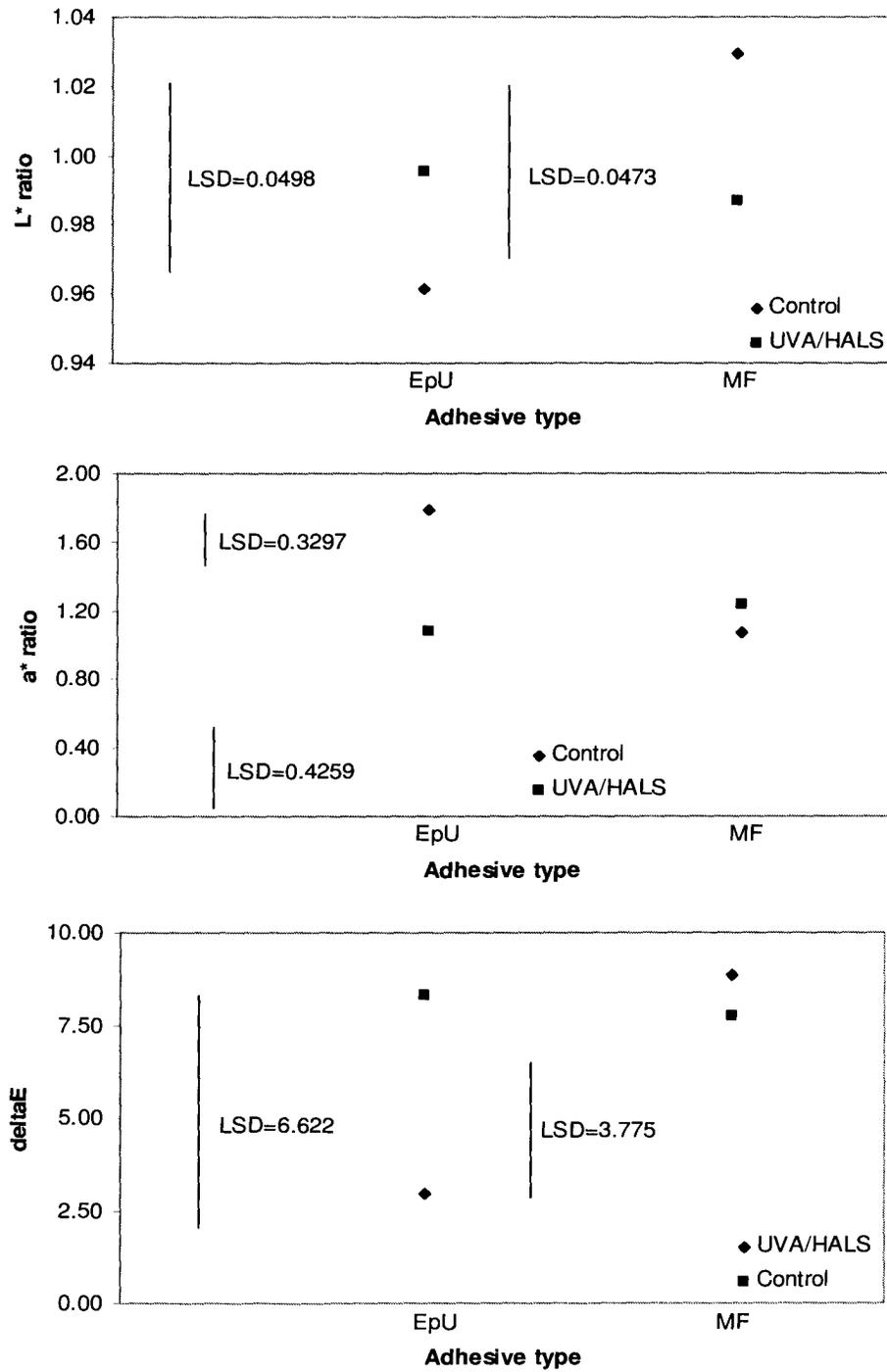
Figure 4.5: Effect of adhesive/stabilizer on L* ratio, a* ratio and deltaE after exposure to solar radiation

The discoloration of dowels in region 1 and 3 before and after exposure to solar radiation was visible to the naked eye. Figure 4.6 and Figure 4.7 show photographs of unstabilized EpU and MF before and after exposure to solar radiation, respectively.
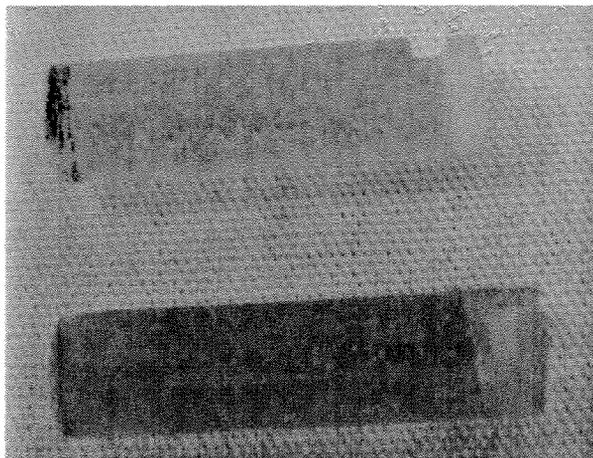
Figure 4.6: Unstabilized EpU before (top) and after (bottom) exposure to solar radiation
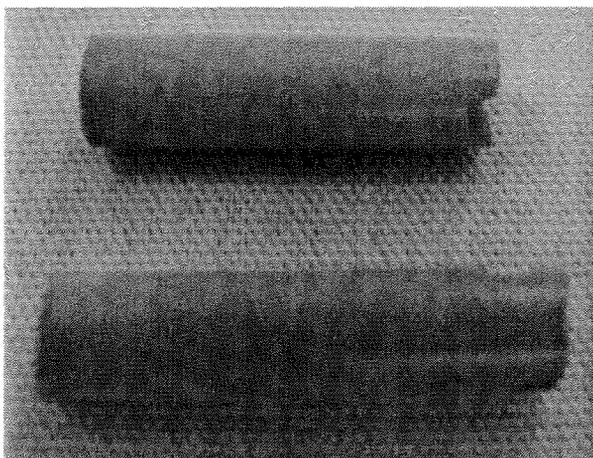
Figure 4.7: Unstabilized MF before (top) and after (bottom) exposure to solar radiation

4.3.3 Morphological Changes

A confocal profilometer was used to visualize erosion along the length of each dowel to determine whether degradation was greater at the interface where the adhesive was exposed to both wood and solar radiation (as hypothesed in the introduction). Figure 4.8 and Figure 4.9 show profileometry plots for MF and EpU surfaces (9 mm^2) across the interface (region 2), respectively. Greater deterioration at the interface would appear in the centre of the images. For both adhesive types this pattern of degradation was not observed.
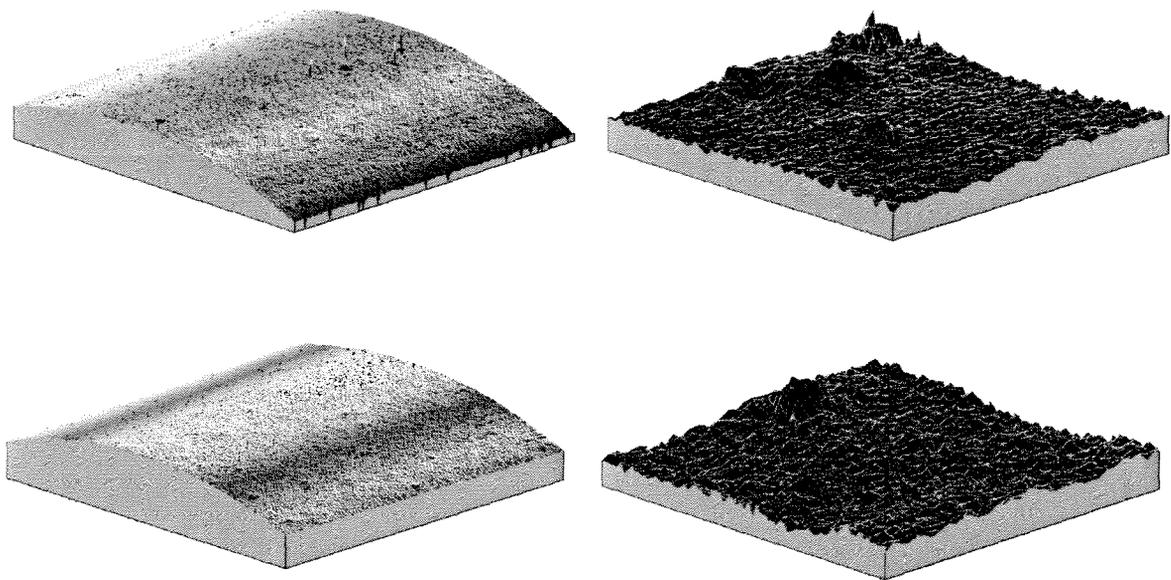
Figure 4.8: Unstabilized MF before (top) and after exposure (bottom)
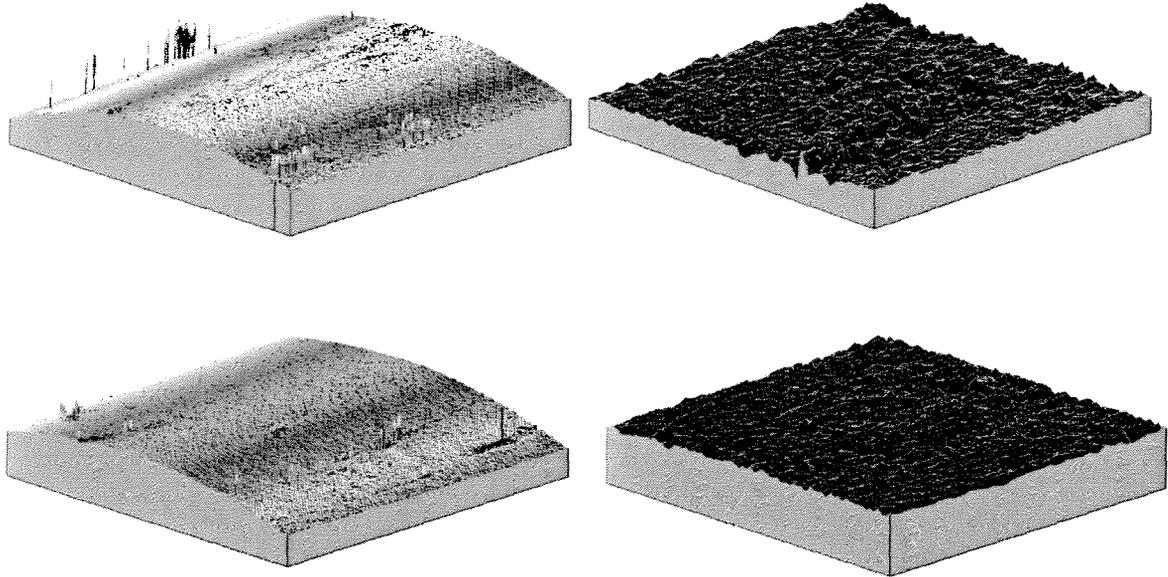
Figure 4.9: Stabilized EpU before (top) and after exposure (bottom)

A scanning electron microscope (HITACHI S-2600N) was used to investigate structural characteristics at the surface of the unstabilized adhesive dowels after exposure. Figure 4.10 and Figure 4.11 show SEM images of unstabilized MF and EpU dowels after exposure to solar radiation, respectively. Besides a few scratches on the surface of the adhesive dowels, probably resulting from removing the glass tubes, no evidence for distinct erosion in region 2 was found.
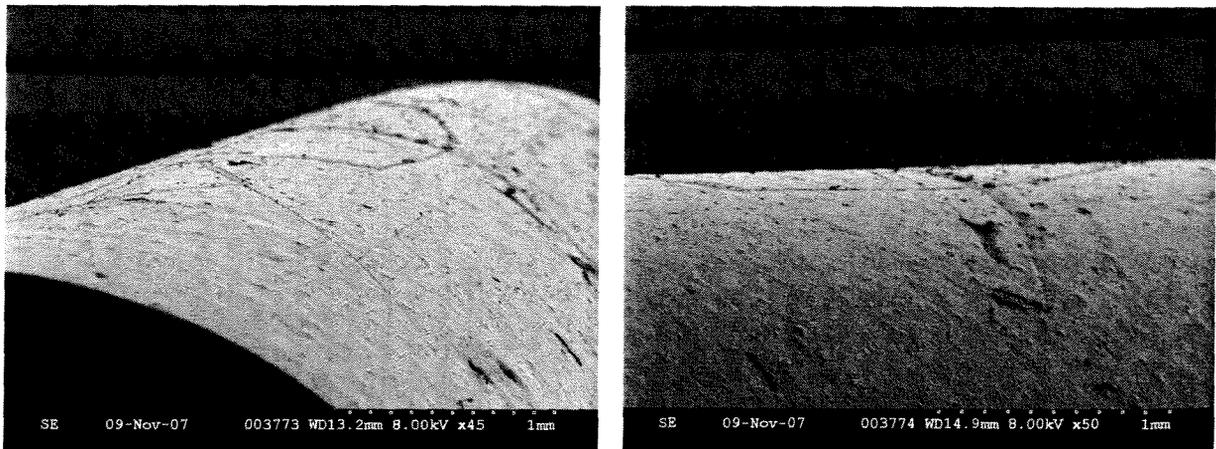
Figure 4.10: Unstabilized MF after exposure to sunlight. Complete dowel (left), interface region (right)
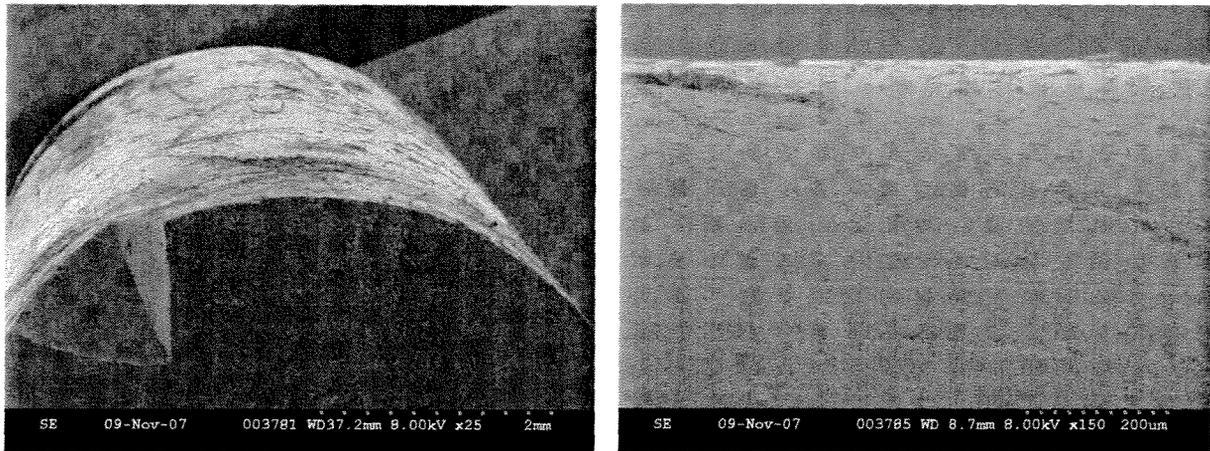
Figure 4.11: Unstabilized EpU after exposure to sunlight. Complete dowel (left), interface region (right)

4.4 Discussion

There were no significant changes in the color (deltaE) of the part of the adhesive dowel that was fully inserted into wood (region 3). In contrast, the part that was exposed to light (region 1) showed significant color changes, as expected. Nearly all exposed adhesive dowels also showed visible color changes a few millimeters below the surface of the wood. This is probably due to penetration of light through earlywood causing chemical changes and discoloration. Nevertheless, results didn't appear to support the hypothesis that wood catalyzed the photodegradation of the adhesives. Severe degradation resulting in increased interfacial surface roughness was not observed with any adhesive specimens exposed to 200 hours of sunlight (Figure 4.2). It is possible that the duration of exposure (200 hours) of the samples to solar radiation was not long enough to observe the hypothesed phenomena. However, the exposure period couldn't have been easily extended, due to seasonal changes in the weather towards the end of the trial resulting in longer and more frequent rain periods. Other researchers have exposed polymer samples in their weathering experiments for more than 1000 hours (Stark and Matuana 2006), but Decker, Zahouily, and Valet (2001) reported that distinct changes in IR spectra can be observed after only 200 h of QUV exposure. FTIR analyses of adhesive dowels using a Perkin Elmer Spectrum One FTIR Spectrometer, didn't give any meaningful results, which was probably due to the difficulty of making a FTIR measurements on a cylindrical shaped adhesive dowel.

It is known that the use of a benzotriazole UV absorber in combination with a hindered amine light stabilizer is capable of protecting many polymer compositions (Renz et al. 2001). The stabilizer in this experiment was effective at restricting the discoloration of EpU samples from photodegradation, but not the MF adhesive dowels. This accords with the results in Chapter 3, and suggests that other types of stabilizers might need to be added to MF adhesives to increase their photo-resistance. Clough et al. (1996) mentioned that stabilizer formulations which protect polymeric materials against discoloration need to be individually optimized in order to obtain the lowest possible extent of discoloration for each polymer. Therefore, findings here are not surprising. Other additives beside the UVA/HALS stabilizer weren't added to any of the adhesives tested here. Impurities from processing however can be responsible for absorbing UV light and thus causing severe discoloration of polymers (Searle 2000) It is possible that the light stabilizer used here was not able to absorb/scavenge all of the light and free radicals that caused discoloration of the MF adhesive

Kaci et al. (1999) mentioned that the HALS, Tinuvin 783, was effective at restricting the rates of formation of ketones in low density polyethylene (LDPE), which are involved in photochemical reactions due to photon absorption by its carbonyl group (Kaci et al. 1999). Stabilized MF adhesives showed more chemical modifications upon QUV aging than urethane adhesive (Decker, Zahouily, and Valet 2001). According to these researchers (Decker, Zahouily, and Valet 2001) ether cross-links in MF adhesives are sensitive to photodegradation, which is seen as a decreased ether peak around 1070 cm^{-1} (see Chapter 3). Another light stabilizer product needs to be found which improves the photostability of MF adhesive.

As described earlier in this chapter, EpU and MF dowels were labeled from the bottom with a permanent marker. The label on EpU samples was bleached after exposure. That was not observed with MF labels. Such bleaching may be attributed to solar radiation because unexposed EpU dowels inserted in wood and stored in a conditioning room didn't exhibit bleaching of labels. The transparency of EpU seems to be responsible for solar radiation reaching all the way through to the bottom of the dowel. This bleaching effect was observed in the previous experiment in Chapter 3 where samples were exposed to UV light. If UV light is capable of penetrating through the dowel, then it is apparent that the UV absorber that was added to the dowels was not able to fully protect the clear EpU adhesive. Hence it might be desirable to pigment

glues used in wood composites exposed outdoors to match the color of wood rather than use clear glue lines.

4.5 Conclusions

The hypothesis that adhesive photo-degradation is catalyzed by wood photodegradation, could not be supported by the experiment performed in this Chapter. Profileometry didn't reveal erosion of the adhesive at the interface where dowel samples were exposed to both sunlight and wood. This finding might be due to lack of intimate contact between wood and adhesive at a molecular level. Alternatively, the exposure time may have been too short for the hypothesed effect to have occurred. The stabilizer was effective at restricting discoloration of EpU dowel samples, but it was less effective with the MF dowel samples.

5. General Discussion and Conclusions

5.1. Discussion and Suggestions for Further Research

In this thesis it was hypothesed that photodegradation of adhesives is catalyzed by photodegradation of wood. Initial experimentation in Chapter 3 was performed to evaluate the performance of adhesives under artificial weather conditions; these results were also used to select adhesives for the second experiment (Chapter 4), which attempted to answer the hypothesis. The stabilized and unstabilized adhesive dowels didn't show distinct surface erosion in the region where they were in contact with wood and exposed to solar radiation for 200 hours. Hence, the results in Chapter 4 don't support the hypothesis that adhesive photodegradation is catalyzed by photodegradation of wood. Nonetheless, arguments were made in Chapter 4 which indicate that the experimental results may have been due to lack of intimate contact (at the molecular level) between adhesive and wood or due to the limited exposure time. Therefore, further refinement of the experimental methodology would be desirable to test the hypothesis advanced in this thesis.

The experiments performed in Chapter 3 to test the photostability of different adhesive types and the photostabilization of adhesives with UVA/HALS additive yielded interesting results. The EpE adhesive was outstanding in terms of weight loss, tensile strength performance and lack of discoloration. The stabilizer was effective at restricting discoloration of EpE specimens, but it did not affect weight loss of samples exposed in a QUV weatherometer. Therefore it would appear that chemical changes in EpE samples, resulting in discoloration, did not cause significant physical degradation of the adhesive. MF adhesives are less durable outdoors than resorcinol formaldehyde adhesives (Petrie 2007), but the MF adhesive showed the 2nd best strength results. However, the MF adhesive had the highest weight loss, and second largest discoloration. The stabilizer was ineffective at restricting discoloration of the MF adhesive, but effective at reducing weight losses. The thermoplastic/thermoset EPI adhesive showed relatively low weight loss (2nd best overall) and the largest discoloration, and strength losses. A water-based polymer isocyanate adhesive used for plywood has shown bond durability that is comparable to phenolic adhesives (Yoshida 1986). However, after 36 months of natural weathering the water-based polymer

isocyanate lost most of its initial bond quality (Yoshida 1986). The EPI appears to be less suitable for glulam exposed outdoors than the other adhesives tested here. For glulam applications structural adhesives are usually required with high strength properties and performance levels that do not change significantly with moderate aging (Petrie 2007). As mentioned by Petrie (2007) structural adhesives are generally thermosetting types with a higher degree of chemical cross-linking. Mynott and Van der Straeten (1984) pointed out that resorcinol formaldehyde and resorcinol phenol formaldehyde adhesives are currently dominating the field of structural wood gluing. They have been shown to be at least as durable as the wood itself under exterior exposure conditions (Petrie 2007). Epoxides have been used for some specialized applications such as metal-to-wood bonds (Petrie 2007). According to Frihart (2005) they are less commonly used in wood bonding because they cost more than most wood adhesives. The clear EpU adhesive tested here exhibited characteristics, which make it a potential candidate for use in wood composites used outdoors, such as glulam beams. The EpU showed relatively little discoloration after 200 hours exposure in the QUV device. This lack of discoloration may be important in composites, where a clear gluline is required. The EpU adhesive was unusually elastic which doesn't allow its strength characteristics to be compared with those of the other three adhesives tested here. A rather flexible adhesive is more capable of accommodating wood's dimensional changes, whereas other adhesives often become brittle after exposure (Zeus Industrial Products 2005, Shangguan et al. 2006). Mynott and Van der Straeten (1984) found that the shear strength of epoxide bonded joints in glulam beams didn't decrease significantly after 10 years of weathering, but nevertheless the capability of the EpU adhesive to bond wood exposed outdoors will have to be investigated separately. Also the economics of using EpU adhesive for glulam beams will have to be studied. Based on the results described in this thesis all adhesives possessed some interesting properties for gluelam beams exposed outdoors, but the EpE and EpU appeared to have the greatest potential.

Results in both Chapter 3 and Chapter 4 revealed that stabilized EpU showed far less discoloration than stabilized MF samples. According to Dorn and Breuel (1992) the performance of specific adhesive types tested under certain weather conditions are not necessarily applicable to other polymers. For example, Turton and White (2001) investigated the photodegradation of two stabilized polypropylenes, and found

surprising differences in their tensile strength performance after weathering. Decker, Zahouily, and Valet (2001) found that stabilized urethane adhesive showed less discoloration than stabilized melamine adhesive exposed under the same conditions. The discoloration of EpU was greatly restricted by adding a UV stabilizer (UVA and HALS) to the adhesive; whereas the same stabilizer formulation was not effective at reducing the discoloration of the MF adhesive. Some stabilizers are also known to affect the color of polymers (Pospisil et al. 2002). Phenolic stabilizers are colorless in their original form and their architecture combines intrinsic activity with physical persistence (Pospisil 2002). Pospisil (2002) mentioned that polymer discoloration can be due to the formation of quinone methides, which can be formed due to trapping of alkylperoxy radicals by phenolic stabilizers. The type and number of radicals created in a polymer during exposure are quite specific and may vary due to different chromophore types and amounts in the polymer and also different chemical compositions of the adhesive backbone. HALS protect polymers by free radical scavenging, and their stabilization reactions are not completely understood (Rabek 1987, Horsey 1994). It is possible that differences in the discoloration of stabilized EpU and MF adhesives during exposure to light might be related to the effectiveness of the HALS at scavenging radicals in the two adhesives. Hence, further research to examine this would be desirable. Furthermore it would be beneficial to determine the best stabilizer formulation for the different adhesives. As glulam beams gain greater importance for outdoor use, this questions may become increasingly important.

Stabilized MF samples experienced less discoloration when exposed only to solar radiation (Chapter 4) compared to samples exposed to light and moisture in a QUV weatherometer. The synergistic effect of moisture and UV light in degrading polymers is well documented in the literature (Searle 2000, Kockott 1989). Moisture changes in polymers can cause swelling and shrinking. Solar radiation can cause embrittlement of the material surface, which means that the tendency of the polymer to crack under swelling/shrinking stresses is further promoted. Subsequently, cracks promote deeper penetration of light into the polymeric material, resulting in severe polymer degradation (Kockott 1989). Furthermore, Kockott (1989) pointed out a synergistic effect of short-wave radiation, water, and air-oxygen on the discoloration of polymers such as titanium-dioxide pigmented coatings. Therefore findings here accord with results in the literature.

5.2. Conclusions

The EpE adhesive showed the best overall performance after exposure to 200 hours to artificial weathering. A stabilizer (UVA/HALS) was effective at reducing the weight loss of the MF adhesive and was effective at reducing discoloration of the epoxy adhesives. The stabilizer was ineffective at restricting weight losses of EpE, EpU and EPI adhesives and not effective at reducing discoloration in the cases of MF and EPI adhesives. Therefore, it can be concluded that the stabilizer formulation needs to be tailored to suit different adhesives. QUV exposure degraded the MF and EpU adhesives more than Xenon-arc exposure. The synergistic effect of moisture and UV radiation on the degradation of adhesives may account for this observation. Profileometry didn't reveal more distinct erosion of the adhesive at the interface where dowel samples were exposed to both sunlight and wood, as hypothesed. A lack of intimate contact between wood and adhesive at a molecular level or the limited exposure time may be responsible for this observation. Based on these findings it can be concluded that EpE and EpU might be good candidates for glulam beams exposed outdoors, and MF adhesive only if it is stabilized.

6. References

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Appendix 1

Statistical Analysis – Chapter 3

Effects of adhesive type, stabilizer, and adhesive stabilizer interaction on color (deltaE, L*, a*, and b*), tensile strength and weight loss (see CD)

Appendix 2

Statistical Analysis – Chapter 4

Effects of adhesive type, stabilizer, and adhesive stabilizer interaction on color (deltaE, L*, a*, and b*), and surface roughness (see CD)