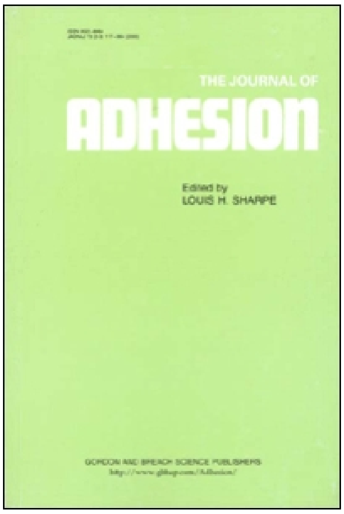

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A Review of Adhesion Promotion Techniques for Solid Timber Substrates

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The use of primers, coupling agents, and other surface treatments to enhance adhesion is now common in the aerospace, automotive, and plastics industries, where they are used to develop highly durable bonds to metals, advanced composites, ceramics, and plastics. However, such treatments are virtually non-existent in the wood products industry although they could solve important adhesion problems. In particular, adhesion promoters can enhance the environmental durability of epoxy bonded joints, and they can enhance the reliability of bonds to timber treated with wood preservatives. A review of current findings is provided that attempts to gather the scarce and disperse information available in the literature about adhesion promotion techniques for bonded solid timber joints. A general overview of the research needs on this topic is also given.

Keywords: Adhesion promoters; Durability; Solid timber; Surface treatments

1. INTRODUCTION

Long-term environmental durability is one of the most important requirements of bonded joints. Although the degradation of the bond is likely to be inevitable, there are means by which to slow down the process. Proper design of a joint or structure is necessary to maximize

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long-term durability, and design can be used to protect bondlines from aggressive environments. Traditional methods of improving durability involve slowing down the degradation mechanisms, but other methods that provide additional adhesion mechanisms (*e.g.*, primary and/or physical bonds that are less susceptible to degradation) can be used to increase durability [1]. These include the use of primers, coupling agents, and other surface treatments. Despite the extra cost associated with them, their use is of particular value where structural bonds may be subjected to repeated wetting and drying [2].

2. SURFACE TREATMENTS

2.1. Corona Discharge Treatment

Corona discharge treatment is a variation of plasma treatment. Plasma has often been referred to as the fourth state of matter and is composed, typically, of a large concentration of highly excited atomic, molecular, ionic, and radical species. The positively charged particles and negatively charged electrons exist at almost the same electrical density, so the matter is overall electrically neutral. Matter can be ionized by raising the internal energy content. Consequently, the plasma state can be created under the action of thermal, electrical, mechanical, nuclear, or radiant energies [3,4].

Plasmas can be classified either as: equilibrium plasmas (also called thermal or hot plasmas, with high degrees of ionization) or non-equilibrium plasmas (also named non-thermal or cold plasmas, with low degree of ionization). In equilibrium plasmas, the temperature of electrons and of the gas are the same, and can be as high as 10,000°C. In non-equilibrium plasmas the gas is at ambient temperature, but the temperature of electrons is very high, of about 10,000°C [3,4].

Cold plasma is a partially ionized gas composed of a complex mixture of electrons, ions of either polarity, neutral atoms and molecules, free radicals, photons, and excited species in lower or higher energy states. Plasmas lose energy to the surfaces which limit them through radiation and conduction processes, and through chemical reactions and phase transformation events. Consequently, to sustain the plasma state, energy must be continuously injected into the system. The easiest way to assure this requirement is by using electrical energy [4,5].

The non-equilibrium plasmas are classified roughly into two categories: (a) ordinary low-temperature plasmas generated at low pressure, also called "glow discharge", and (b) corona discharges at atmospheric pressure [3].

Glow discharges are the most widely used technique for low-temperature plasmas. The reason is that the mean free path of activated gas molecules is longer in vacuum, which allows the use of a bigger distance between the electrodes and the samples. This kind of plasma has been used since the late 1960s as a highly effective pretreatment for the surface preparation of low surface energy polymers for adhesive bonding. Such polymers include low- and high-density polyethylene, poly(4-methylpent-1-ene), poly(vinyl fluoride), poly-(vinylidene fluoride), fluorinated ethylene-propylene copolymer, polyacetals, polyamides, poly(ethylene terephthalate), polystyrene, polycarbonate, etc. This technique has also been applied successfully to silicone rubbers and other difficult-to-bond rubbers [3,5].

The corona discharge treatment (CDT) has a more restricted application range, since it is limited both to the materials that are responsive to this method of surface preparation and the material configuration itself. Complex shapes cannot easily be treated because the treatment quality is a function of the distance of the surface to the electrode. Also, since corona treatments are normally conducted in ambient air, they can be affected by environmental changes in the location where it takes place. The main advantages of corona discharge treatments are that, since no vacuum system is needed, the equipment investment is much lower than for ordinary low temperature plasma installations and, with this kind of treatment, it is possible to treat large surface areas. Therefore, corona discharge treatment is also a long established method for treating polymers prior to adhesive bonding, printing with inks, lamination to other films, vacuum metallization, etc. [5].

In corona discharge treatment, the discharge is generated by applying a high frequency, high voltage signal to an electrode that is separated from an earthed (grounded) plane, usually by only a few millimetres, by an air gap, the substrate, and a layer of dielectric material (Figure 1). Frequencies in the range of 9 to 50 kHz with peak voltages up to 30 kV are generally used in the corona treatment industry. When the high frequency generator and the step-up high tension transformer applies a high voltage to the electrode, virtually no current will pass through the air gap until the electrical breakdown of the air takes place, ionizing the air and, thus, creating a plasma. This occurs when the voltage across the air gap reaches a level of 3000–5000 volts per millimetre, the variance being caused by ambient conditions such as air humidity. At breakdown potential, free electrons are accelerated towards the positive electrode with such high energy that they are capable of displacing electrons from molecules in the air gap. The consequence is an avalanche effect, with electrons and

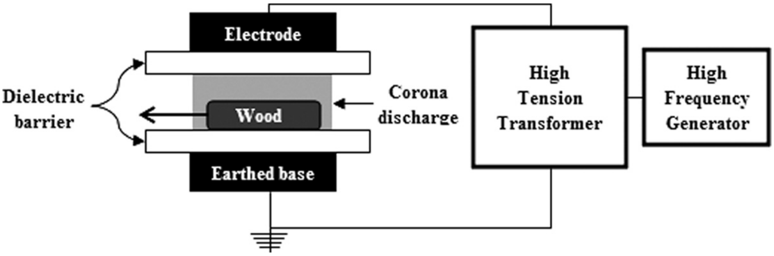

FIGURE 1 Schematic of corona discharge equipment.

the corresponding ions being produced, resulting in current flow across the air gap. Apart from using air as the medium in which the plasma is generated, liquids or oxygen-containing gases are often injected into the air gap in an attempt to increase treatment efficiency [3,5].

The selection of the corona treatment equipment and process parameters, *e.g.*, power output to the discharge, electrode separation, air flow rate, sample temperature, treatment time, and cooling rate, influences the effectiveness of the treatment. From all these factors, it has been found that the power output and treatment time have the strongest effect on the treatment efficiency. The treatment time in the air-gap has a minimum value, below which the residence time is shorter than the oxidation initiation time and, at that point, oxidation is negligible and adhesion levels will not improve. Adhesion also deteriorates if the treatment levels are too high and lead to the degradation of the material. For each case an optimized routine must be developed and adopted [5,6].

The analytical methods commonly used to evaluate treated surfaces are wettability measurements, infrared spectroscopy, x-ray photoelectron spectroscopy (XPS), high-resolution electron loss spectroscopy (HREELS), and microscopic observations (atomic force microscopy, AFM; scanning electron microscopy, SEM; etc.). The use of time-of-flight secondary ion mass spectrometry (TOF-SIMS) can clarify the chemical structural changes in the surface region, but the literature on the application of this technique deals only with ordinary low-temperature plasma treatments and not very extensively [5].

Corona-induced surface activation has been used extensively to improve adhesion and to modify surface characteristics of polymers, especially synthetic, but less experimental data is available on the activation of natural polymeric surfaces (lignocellulosic materials, etc.). This can be explained by the inherent surface characteristics of these materials. Timber surfaces are complex and variable, with low surface energy. Wood having a moisture content ranging from 10 to 15% acts as conductor with an electrical conductivity of approximately 1 CΩ/cm, and this enables the treatment of timber veneers or even boards up to 30 mm thick [7,8].

Some studies on the subject are presented hereafter in order to give an idea of the actual knowledge of timber treatment with the corona technique.

Uehara and Jodai (1987) [9] found that the joint strength of corona-treated apitong (*Dipterocarpus grandiflorus* Blanco) bonded with urea-formaldehyde (UF) adhesive increased with the corona treatment (34 kV, 30 kHz, gap between electrodes 5 mm). They also found that the wettability (for water, glycerine, and UF resin) and bondability increased with an increase in the degree of treatment up to an optimum degree of treatment, but from that point onward there was a decrease in the bondability. The best degree of treatment was 0.533 kW min/m^2 with a rate of 1.5 m^2/min. However, for the phenol-resorcinol-formaldehyde (PRF) resin the results were different. After the treatment the wettability by the PRF resin was not improved and the bond did not show an improvement in joint strength.

Furuno and Uehara (1990) [10] investigated histochemically corona treated heartwood specimens of hinoki (*Chamaecyparis obtuse* Endl.) and buna (*Fagus crenata* Blume), by using reduction with a sodium borohydride ($NaBH_4$) solution and Schiff's staining method in combination with infrared (IR) and SEM to detect aldehyde groups produced after a corona treatment (15 kV, 60 Hz, gap between electrodes 4 mm, 1 and 2 hours treatment). They concluded that there was an increase in the number of aldehyde groups on the timber surface with the corona discharge for the edge-grain specimens. In the case of end-grain specimens, the treated surface has open capillaries, so that the proportion of electrons colliding against that surface is smaller than for the edge-grain specimens, leading only to a slight increase in the number of aldehyde groups.

Back (1991) [11] studied the effects of the corona discharge on the wettability of teak, birch, and pine (*Pinus sylvestris* L.). The contact angles of water 10 seconds after treatment (12 kJ/m^2) showed that there was a significant increase in the wettability of teak and birch, but the effect on pine was minimal with the method and parameters used. He concluded that corona discharge can be used to treat high resin or oil content timbers and to treat wood surfaces that have aged due to heating.

Sakata *et al.* (1993) [12] have shown that the treatment of the surface of several softwood, hardwood, and tropical wood veneers by corona (500 W and 16 kV at 5 kHz; gap between electrodes 3.2 mm; distance from the electrode to the specimen surface 1.0–3.3 mm; number of passes 1; speed of treatment variable) caused a considerable increase in the wettability of the surface by the urea resin and, consequently, in the bondability of the veneers with water-based adhesives. Negligible chemical effects of the treatment on the wood surface main components (cellulose, hemicellulose, and lignin) were observed with the dye-adsorption method. On the other hand, the treatment affected the alcohol-benzene extractives and oxidized them to produce aldehyde groups. The neutral fraction of the extractives was the most affected. They concluded that an increase in the wettability of corona-treated wood veneers resulted mainly from the oxidation of the highly hydrophobic surface layer of the neutral fraction substances in the extractives and from the reduction in their hydrophobicities. The effect of the degree of corona treatment on the bond (using a mixed resin of urea-formaldehyde and poly(vinyl acetate) emulsion at a ratio of 1:2) tensile strength, was that the joint strength increased rapidly after the initial mild treatment of corona, but then steadily (isunoki) or gradually decreased (purpleheart) with treatments more energetic than $250\,\mathrm{W}\cdot\mathrm{min/m^2}$.

Podgorsky *et al.* (2000) [13] used corona discharge treatments on oak and measured its effects through contact angles measurements carried out with glycerol. The gas temperature of the discharge was measured at discharge gaps of 1, 2, and 3 mm. The temperature was measured 60 seconds after ignition of the plasma (time necessary for the gas to reach the equilibrium temperature). Temperatures of 35°C were measured for the three gap distances at a wood velocity of 1.5 m/min such that the plasma did not induce any thermal influence on the wood surface (pyrolysis effects appear above 120°C). Their main conclusions about the experimental parameters were that the higher the corona voltage, the lower the contact angle (9 kV, 12 kV, and 15 kV applied during 5 minutes, wettability improvement of 64%, 72%, and 89%, respectively), and the longer the treatment the higher the increase in wettability (9 kV applied during 1, 5, 10, and 30 minutes, wettability improvement of 34%, 64%, 70%, and 80%, respectively). In addition, the corona treatment performed in air (9 kV and 15 kV applied during 5 minutes, wettability improvement of 64% and 89%, respectively) lead to lower contact angles than when using nitrogen as the treatment medium (9 kV and 15 kV applied during 5 minutes, wettability improvement of 39% and 27%, respectively).

Rehn and Wolkenhauer (2003) [8] conducted some experiments on corona discharge treatments on spruce and beech wood specimens. The specimens were planed and then polished with sandpaper (with a grain size of 100). They concluded that the polishing process could be omitted when treating surfaces with corona discharge. The moisture content (MC) of beech wood (3, 7, and 10%) before treatment had no influence on the final result. The discharge gap (4, 6, and 8 mm) had no influence in the results either. Shear strength of bonded teak, robinia, oak, and pine, using the lacquer as adhesive, was improved with corona treatment (shear strength improvement of 4%, 26%, 16%, and 68%, respectively). Delamination resistance of coatings on wetted bonded robinia, spruce, and beech was improved with corona treatment (delamination was reduced by 140%, 200%, and 80%, respectively).

Despite the fact that the results mentioned above are positive and promising for the CDT technique, it should be noticed that they focus on a limited number of adhesives and timbers, and that the wettability tests made involved very few different probe liquids. Therefore, more investigations are necessary to correlate the wettability improvements with the strength of bonded joints for more adhesives and timber types. Besides this, since a by-product of corona treatment is ozone and in recent years legislation has been introduced that places restrictions on its emissions, this is an issue that has to be managed [14,15].

2.2. Flame Treatment

One of the first applications of flame treatment dates back to the early 1950s, and it was used to enhance print adhesion to polymers with low surface energy. Since then this technique has been used in a variety of applications with many different polymers (low-density polyethylene, high-density polyethylene, polypropylene, nylon 11, poly(ethylene terephthalate), poly(vinyl fluoride), ethylene-chlorotrifluoroethylene copolymer, etc.), in some cases replacing corona treatment and in others as a complement, being second only to the CDT in the amount of polyolefins treated per year worldwide [16].

In the early 1990s, advances in burner designs and control systems, increases in line speeds, as well as environmental concerns, led to a resurgence in interest in flame treatment. In the mid to late 1990s, flame technology still lacked the tight controls and repeatability features of corona, mainly due to the process variables such as fuel and air supplies on a day-to-day basis. With the introduction of new, more sophisticated technology, the previous problems were solved and customer interest has grown [5].

It is believed that compared with corona, flame treatment offers benefits such as: higher achievable treatment levels with shorter treatment times; lower treatment decay rates; no backside treatment;

no ozone; no gauge or surface contour restrictions; and surface decontamination of impurities (since the exothermic reaction created in the gas combustion produces ambient flame temperature of 1800°C). Because of these advantages flame ionization is a process used in the plastics and automotive industries to improve the bonding of adhesives and inks to car panels and plastic containers [4,6].

The flame treatment technique is a rapid and effective method for treating many polymers, as long as they have regular shapes as film, sheet, and bottles with cylindrical sides. A variety of functional groups is introduced by the treatment, including hydroxyl and carbonyl groups. This increases the surface energy of the treated polymer surface, which leads to an improvement of its wetting by the liquid phase, *e.g.*, by the adhesive. The depth of chemical modification is only a few nanometres and the treated surface is relatively stable [4,6].

The principle of the flame treatment technique is the use of a flame containing excited ions which oxidise an organic surface. The gas flame results from the combustion between a fuel and an oxidising element, methane, propane, or butane, and air. This combustion produces a complex exothermic reaction, or plasma, during which oxygen molecules disassociate into free oxygen atoms that bombard the material surface. Depending on the application, the plasma can include many energised species: free radicals, ions, neutral species, and electrons, more so O, OH, NH, NO, and CN. However, there is some evidence that suggests that it is the oxygen content which plays the major role in the activation process. Besides the chemical properties, the plasma also shows electron energies of 0.5 eV [17]. Whilst this may be considered low, the high mass flow rate of a flame system will polarise the polymer to depths greater than a single molecular layer. The combination of these chemical and polar charges provides a highly receptive surface for bonding [5,6].

The flame treatment technique is a process which involves passing a substrate under a flame whose physical parameters are strictly controlled (Figure 2). The hydrocarbons and air are well mixed and then reacted. Optimum flame conditions are achieved when combustion reaches the stoichiometric condition whereby sufficient oxygen is supplied to combust all of the fuel gas chemicals in the supply mixture. For example, the complete combustion of 1 mol of methane requires 10 mol of air ($CH_4 + 2O_2 + 8N_2 \rightarrow CO_2 + 2H_2O + 8N_2$), so the stoichiometric ratio for an air-methane flame is 10:1. The stoichiometric ratio for an air-propane flame ($C_3H_8 + 5O_2 + 19N_2 \rightarrow 3CO_2 + 4H_2O + 19N_2$) is 24:1, and for an air-butane flame ($2C_4H_{10} + 13O_2 + 49N_2 \rightarrow 8CO_2 + 10H_2O + 49N_2$] is 31:1. In addition to the hydrocarbon/air ratio, the other variables in the treatment are the total flow of the gases, the

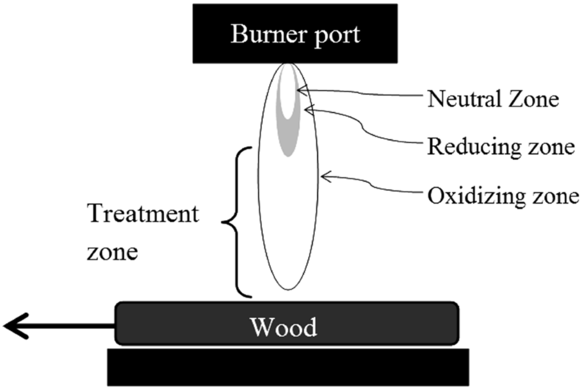

FIGURE 2 Schematic of flame treatment apparatus.

flame geometry, the treatment time, and the position of the polymer in relation to the flame [6].

Although flame treatment has been used in the plastics industry for about 40 years with considerable commercial success, it has not been applied industrially to solid wood substrates. This is probably due to safety concerns that led industry to prefer chemical pre-treatments. The lack of research on this subject contributes to the need for additional fundamental studies, as well as studies involving full-scale process design that includes factors such as safety, environmental aspects, costs, and investment [16].

Nussbaum (1993) [16] showed that flame treatment led to a marked increase in wettability of the tested wood surfaces. For the wettability tests, veneers of teak (*Tectona grandis*), birch (*Betula verrucosa*), and pine (*Pinus sylvestris* L., which was preheated for 5 hours at 95°C before conditioning to create a more hydrophobic surface, *i.e.*, to simulate ageing) were conditioned at 20°C/65% RH before the flame treatment (burner output: 2.0 or 2.9 MW/m^2 burner area; number of passes: 3, 6, 10, 20, or 40; distance from flame tip: 5, 7.5, or 10 mm; speed: 0.2, 0.4, 0.8, or 1.2 m/s). Conditions varied with timber species. After the flame treatments, the specimens were reconditioned at 20°C/65% RH for 2 hours before the wettability measurements with distilled water using the sessile drop method. Darkening or loss in brightness of the veneers was observed only at the lowest speed, 0.2 m/s, and mainly at the edges. The contact angle measurements show a markedly increased wettability on all three wood species after exposure to flame treatment (63% for teak, 69% for birch, and 53% for pine – values obtained with different treatment conditions). The decrease in the contact angles was more pronounced for wood species with low oleophilic content than for species with a higher content at a given treatment level. The optimum wettability was, in general, obtained at a lower energy level and with faster speeds through the flame. The duration of the activation of wettability varied between wood species. Pine and birch showed a progressive increase in the contact angles up to their initial values in a period of several weeks, but with pine presenting always lower contact angles than birch. On the other hand, after only one week the contact angles obtained on teak returned to their initial value. Surface measurements with XPS showed a considerable increase in oxidation level as a result of the flame treatment (hydroxyl and to some extent carbonyl groups were formed). The bond adhesion on flame-treated planed pine sapwood samples was evaluated through tensile shear tests of lap joints. The samples were preheated for 5 hours at 95°C and then flame treated (burner output: 2.9 MW/m^2 burner area; number of passes: 20; distance from flame tip: 10 mm; speed: 0.8 m/s). After the flame treatments, the specimens were reconditioned at 20°C/65% RH for 30 minutes and then assembled with a thin poly(vinyl acetate) (PVAc) glue line. A pressure of 0.05 MPa was applied for 10 minutes. The shear tests were performed 1 week later. No improvement in adhesion after flame treatment was observed in the case of a PVAc adhesive, but there was a decrease of subsequent microbiological activity on the wood surface.

Winfield *et al.* (2001) [18] conducted a study in order to investigate the effect of flame ionization on wood surfaces and its usefulness on the long-term performance of factory finished joinery components for exterior use. The flame was produced with an air:propane ratio of 64:2.75 l/min. The distance from the flame to the sample surface was 6.5 mm. The sample passed through the flame with a constant speed of 0.33 m/s. The number of passes through the flame varied from 6 to 12 according to the timber species. The wood species studied were oak (*Quercus robur* L.), meranti (*Sorea spp*.), and pine (*Pinus sylvestris* L.). The samples were planed or rough sawn and were tested at a moisture content of 12%. The wettability of the surfaces was evaluated through the sessile drop method, using deionized water and diiodomethane. An increase in wettability was achieved by passing the hardwood samples, meranti and oak, under the flame six times (wettability gain of 42% for meranti and 59% for oak). However, no improvement in wettability was obtained with pine, even after 12 passes under the flame. This increase in wettability was only stable for 18/24 h in the hardwoods. Stability was not achieved with the pine samples and the contact angle values continued to increase up to

18 hours. The increase in the total surface energy (48% for oak, 39% for meranti, and 21% for pine) was due to an increase in the polar component, which had more effect on the hardwoods than on the softwoods.

In 1998, the EU FLAME FAIR Project No. CT98–3781 [19] – "Improving the Performance and Adhesion Properties of Wood Coatings with the Use of Flame Ionisation Technology" – examined the specific difficulties associated with the use of flame ionization on wood and wood substrates. Results from this study showed that each wood species has a different response to the flame treatment: (a) improved wettability was relatively easy to achieve for: western hemlock, beech, oak and teak; (b) improved wettability was relatively difficult to achieve for: pine, Douglas fir and iroko; (c) species which showed inconclusive or variable results: meranti and spruce. For instance, pine had an optimum number of 12 passes through the flame. Oak exhibited an optimum wettability in the range from 2 to 24 passes. Meranti showed significant improvements in wettability at and above 12 passes, peaking at 24 passes. Iroko had a good wettability increase with 12 passes. XPS analysis of the wood surface showed that from the non-treated samples of all three species (oak, pine, and meranti), pine had the smallest percentage of hydroxyl groups on the surface. Flame treatment reduced the percentage of C-OH bonds on surfaces of oak and meranti to values similar to those for the untreated pine. This reduction was consistent with the decrease in contact angles/increase in surface energy. The percentage of $O-C-O/C{=}O$ bonds increased after treatment due to oxidation [19].

The fact that flame ionization technology is considered as being simple and cost effective to use, making it easily integrated into a complex in-line manufacturing system with minimum disruption, and its recognized contribution to surface adhesion, would turn this technique into a possible choice for the joinery manufacturing industry to improve the performance of exterior coatings to timber. However, the main conclusion of the FLAME project [19] was that improvements in wood adhesion can be obtained by flame treatment, but the results tend to be species-dependent and highly variable, which do not favour its application in a commercial context.

It is clear that the reliable use of flame treatment to enhance the performance and durability of adhesively bonded structural timber joints is still distant, and more fundamental research is needed to overcome the lack of knowledge in this area and to allow the use of this technique on an industrial scale. The design of a manufacturing system focused only on a small number of timber species, instead of treating a wide range of species together, should also be considered [14,15].

3. ADHESION PROMOTERS

With the development of adhesion science and technology, it has become relatively straightforward to produce adhesive bonds of very reasonable strength between most commonly used materials. A conscious choice of adhesive and application method together with appropriate preparation of the surface will produce a strong bond. Many surface preparation techniques have been employed to achieve high initial adhesion, ranging from removal of surface contamination, to changes in substrate profile, and chemical modification, as already mentioned. However, in some situations durable bonds are more difficult to produce. For instance, while adhesives such as phenolics, resorcinolics, and aminoplastic resins produce durable bonds in EN 1995-1-1 [20] service classes 1, 2, and 3, these resins do not form bonds of adequate durability when bonding some preservative-treated timbers, in situations where significant pressures can not be applied, and when bonding non-wood materials, such as FRP profiles, steel rebars, etc., *e.g.* on-site repair and strengthening of timber structures, where adhesives like epoxies and polyurethanes are preferred; unfortunately these do not produce exterior durable bonds. To overcome this, adhesion promoters could be used to improve the bond durability [21–23].

To improve the bond strength between adhesives and substrate, primers, adhesion promoters, and coupling agents can also be used. A primer is defined in EN 923:2005 [24] and ASTM D907-04 [25] as a coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond. EN 923:2005 does not discriminate between adhesion promoters and coupling agents, and defines them as a substance used in small proportions to increase the adhesion to specific substrates. ASTM D907-04 separates these two agents, and considers an adhesion promoter as a substance used to improve bonding of the adhesive to the substrate; it considers a coupling agent as a molecule, having different or like functional groups, that is capable of reacting with surface molecules of two different substances, thereby chemically bridging the substances. In this paper we will follow the ASTM terminology together with the following additional remarks. Adhesion promoters function by improving the substrate wetting or by secondary bonding through van der Waals forces, dipole–dipole interactions, hydrogen bonding, or acid-base reactions. Due to the nature of the interactions involved, adhesion promoters are only capable of improving initial adhesion between adherends and adhesives. On the other hand, a coupling agent is a compound capable of forming primary chemical bonds with both the polymer and the substrate and, thus, producing a water-resistant bond with enhanced durability, although the reaction with the polymer is not necessarily a prerequisite. Thus, a coupling agent can function as an adhesion promoter, but the reverse is not true [4].

In general, adhesion promoters and coupling agents can be used as pre-treatments or additives. As a pre-treatment, they are used either as a solution in a suitable solvent or solvent mixture or as a formulated primer. Used as an additive, they are incorporated into the adhesive. Both approaches have advantages and disadvantages. The pre-treatment method enables employing a specific agent on a specific substrate, thus achieving optimal adhesion, but it has the disadvantage of introducing a process that may be out of the manufacturer's control, i.e., the performance of the agent may depend on the method of application as much as on the chemistry involved. The additive approach may not be as effective in adhesive technology as it is in surface coating technology. The reason is that the overall rheology of the system may be changed by the agent, thus requiring a re-formulation of the adhesive, *e.g.* amino silanes may also act as curing agents or accelerators in epoxy and polyurethane adhesives, thereby reducing the pot life of the mixed system [21–23].

3.1. Silanes

Silanes have been available commercially for many years, and they are the most commonly used coupling agents. They are used to produce highly durable bonds to glass, metals, advanced composites, ceramics, and plastics in the aerospace, automotive, plastics, and composites industries. They are used routinely in composites where the negative effects of water on the mechanical properties of glass reinforced phenolic and polyester resin based composites are recognized. The commercial glass fibres used in reinforced composites are almost always treated with a coupling agent, capable of interacting with both the organic polymer resin and the inorganic substrate. Such an agent has to ensure that the physical properties of the reinforced material remain relatively unaffected by moisture, and reduce the stress concentration at the interface during thermal cycling [21]. More recently their value in improving the adhesion of surface coatings and adhesives has been investigated; in particular, the improvement in the "wet" adhesion of coatings and adhesives which results from their use [6].

Silanes can be used in four main ways, depending on both the application and the polymer of interest: (1) as pre-treatment primers (surface coatings and adhesives); (2) as pre-treatment for fillers (composites); (3) as formulated primers (surface coatings, adhesives, and composites); and (4) as additives to the organic phase (surface coatings, adhesives, and composites) [23].

Silanes are a group of organo-functional compounds that possess dual reactivity. They have the general structure $(RO)_3$–Si–R′–X, where silicon (Si) is the centre of the silane molecule, which contains an organo-functional group (RO) with a second functional group (X). RO is a hydrolysable group, typically methoxy, ethoxy, or acetoxy, which reacts with water to form silanol (Si-OH) and ultimately forms an oxane bond (Si–O–Substrate) with the inorganic or organic adherend. X is an organo-functional group, such as amino, epoxy, or methacrylate, which attaches to the organic resin. R’ is typically a small alkylene linkage [21].

The reactions of interest in silane coupling for an inorganic surface and an organic resin are summarized in Figure 3. The silanes are generally applied from dilute aqueous solutions, partial hydrolyzates, or organic solvents (generally alcohol), and most have undergone initial hydrolysis (Reaction A) to give the corresponding silanols, which ultimately condense to siloxanes through oligomerization (Reaction D) prior to interacting with the chosen substrate. Both reactions are strongly dependent on pH, but under optimum conditions the hydrolysis is relatively fast (minutes), while the condensation reaction is much slower (several hours). Higher alkoxysilanes hydrolyze very slowly in water because they are strongly hydrophobic but, even in homogeneous solution in water-miscible systems, they hydrolyze more slowly than the lower alkoxysilanes. The silanes may interact with the substrates initially through hydrogen bonding (Reaction B) to surface

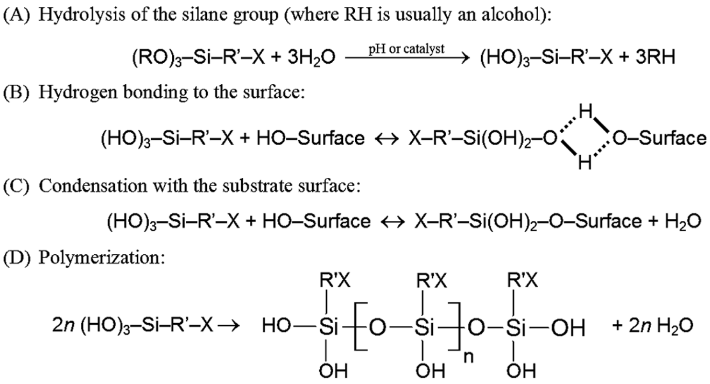

FIGURE 3 Silane coupling reactions [4].

hydroxyl groups, with subsequent condensation reactions of the silanol groups of the coupling agent with the hydroxyl groups of the mineral surface, originating siloxane structures during drying operations (Reaction C). It is also possible, in some systems, that lateral polymerization occurs without the formation of the bonds to the surface. The siloxane film formed on the substrate then consists of multiple layers.

The use of silane coupling agents with composites, mineral substrates, metals, and with polymers is well known. Several mechanistic theories of adhesion promotion have been described, namely: chemical bond; deformable layer; surface wettability theory; restrained layer; reversible hydrolytic bond; and oxide reinforcement. In addition to the stated theories there are another two mechanisms that can be important, namely, inter-polymer networks/chain entanglement and acid-base reactions [4]. A more detailed account of the mechanisms and the main functions of the organo-functional group (RO) and the second functional group (X) of several silanes can be found in Plueddemann (1992) [21].

Several studies conducted on inorganic surfaces have shown that the nature of silane films on metals and glass and their correspondence to the bond performance is complex. Films deposited from non-polar solvents are relatively thick (>1000Å) and resistant to desorption, and films from polar solvents are generally thinner (< 1000Å) and easily disrupted by polar solvents. In practice, an adsorbed silane film on either glass or metals is discontinuous and consists of discrete agglomerates, and each agglomerate can consist of different strata: a silane interface with covalent bonding, a relatively cross-linked intermediate layer, and a superimposed layer of relatively uncross-linked material. The molecular structure of silane films depends to a great extent on the pH of the solution from which it was deposited. Besides, deposited films with similar structures can have different performances, due to the different orientation of silane molecules at the substrate surface. Moreover, the age of the solution from which the silane is deposited, silane concentration, presence of soluble catalytic salts, temperature, and curing conditions on adsorption play also a role in the bond performance [21,26–29].

The only studies found in the literature regarding the treatment of lignocellulosic material with silanes refer to their use to enhance wood properties such as cell wall bulking, anti-swelling efficiency, moisture uptake, and durability [30–33]. No studies were found concerning their use to improve adhesion to timber, or that explain their mechanism of interaction with wood.

3.2. Hydroxymethylated Resorcinol

The use of adhesion promoters and coupling agents is not common in the wood products industry, since water-based, polar wood adhesives as phenolics, resorcinolics, and aminoplastic resins perform quite well on neat wood. However, epoxy adhesives are an exception because they develop dry bonds to wood that are as strong as the wood itself, but once they are exposed to severe stresses of repeated water soaking and drying cycles, the epoxy bonds delaminate and fail to meet requirements for structural wood adhesives intended for exterior exposure [34–37].

Several attempts have been made to improve epoxy adhesive-bonded joint performance. In the late 1950s it was found, for instance, that curing epoxy adhesives made from epichlorohydrin and bisphenol-A (BPA) at 71°C improved water resistance compared with that achieved with cure at ambient temperature, although the improvement was not enough to match the water resistance of a joint bonded with a resorcinol adhesive [38,39]. In the early 1960s, special epoxy adhesive formulations were also developed, such as the Forest Products Laboratory (FPL) Formula 16 adhesive, made from Shell's Epon 828® epoxy resin and diethylenetriamine hardener which contained a titanium dioxide filler and a specially blended lacquer thinner as diluent. This adhesive appeared to be capable of withstanding severe exposure conditions, but long-term exposure tests were never reported [38,39]. The Weyerhaeuser Company in cooperation with Dow Corning, in the late 1960s, developed two epoxy adhesive formulations that, combined with the use of a primer of 2% aqueous solution of polyethylenimine, produced durable epoxy bonds to wood, which performed better than similar bonds made with PRF and phenol-formaldehyde (PF) adhesives, when subjected to either accelerated ageing in an automatic boil test or to 11 years of exterior exposure. Unfortunately, in spite of the promising results, the work was discontinued and the findings were discarded [38,39].

More recently, the continuing need for structural epoxy adhesives with greater water resistance led the Forest Products Laboratory to explore adhesion promoters to improve the durability of BPA epoxy bonds to wood. Their exploratory work led to the discovery of a hydroxymethylated resorcinol (HMR) adhesion promoter that seemed to bond chemically to both epoxy adhesive and lignocellulosics of wood producing joints that were resistant to delamination. HMR is equally effective at enhancing adhesion of other thermosetting wood adhesives, including PRF, emulsion polymer isocyanate (EPI), polymeric methylene diphenyl diisocyanate (pMDI), melamine-formaldehyde

(MF), melamine-urea-formaldehyde (MUF), and UF resin adhesives [35,36,38–41].

The HMR adhesion promoter is used by applying it from a dilute solution at room temperature onto the wood surface before bonding with epoxy adhesives. Several studies [34–36,38,42–44] conducted on two softwoods (Sitka spruce and Douglas fir) and two hardwoods (yellow poplar and yellow birch) led to the development of the best procedure to produce and apply the HMR. The HMR is usually prepared by reacting formaldehyde with resorcinol in a 1:5 molar ratio at mildly alkaline conditions. The typical ingredients are presented in Table 1. The chemicals of the HMR are quite reactive, so it is believed that the solution consists of mono-, di-, tri-hydroxymethyl resorcinol with a few dimers, trimers, or higher oligomers, which condense as the reaction period increases. Because of that, the reaction time (the time between preparing the solution and applying it to the wood surface) determines the molecular size distribution and reactivity of HMR. Experiments have shown that reaction time has a strong influence on the durability of adhesion, in the sense that as the polymerization proceeds fewer HMR coupling sites become available to promote the adhesion between the timber and the epoxy adhesive. For the 5% aqueous solution it was found that the solution should react for a minimum of 3 to 4 h, but not more than 8 h, at room temperature, before use. Dodecyl sulphate sodium salt (0.5% by weight) is added to this mixture at the end of the reaction time to aid wetting of the wood surfaces. After this, the solution is spread on the wood surface at 0.15 kg/m^2. Before bonding with epoxy adhesives, water from the applied HMR must be evaporated or be absorbed by wood, since water interferes with epoxy adhesion to wood, so the primed wood surfaces should be conditioned at 23°C and 50% RH for 24 h before bonding [36].

The original mechanism of wood adhesive bond enhancement proposed by Vick *et al.* (1995) [36] to describe the coupling action of

TABLE 1 Hydroxymethylated Resorcinol Adhesion Promoter Ingredients

HMR ingredient	Percentage by mass
Water, deionized	90.43
Resorcinol, crystalline	3.34
Formaldehyde (aq., 37%)	3.79
Sodium hydroxide, 3 molar	2.44
Total	100.00

HMR was based on organic chemistry reactions and focused on only a single adhesion bonding theory (covalent bonding). According to this mechanism, covalent and hydrogen bonding of HMR between BPA epoxy adhesive and lignocellulosics of the wood would occur (Figure 4). The functional hydroxyl groups formed along the epoxy chains at position (5) would be capable of condensing with the hydroxymethyl groups of the HMR to form ether linkages between the adhesion promoter and the epoxy resin. The other available hydroxymethyl groups of the adhesion promoter should be capable of forming

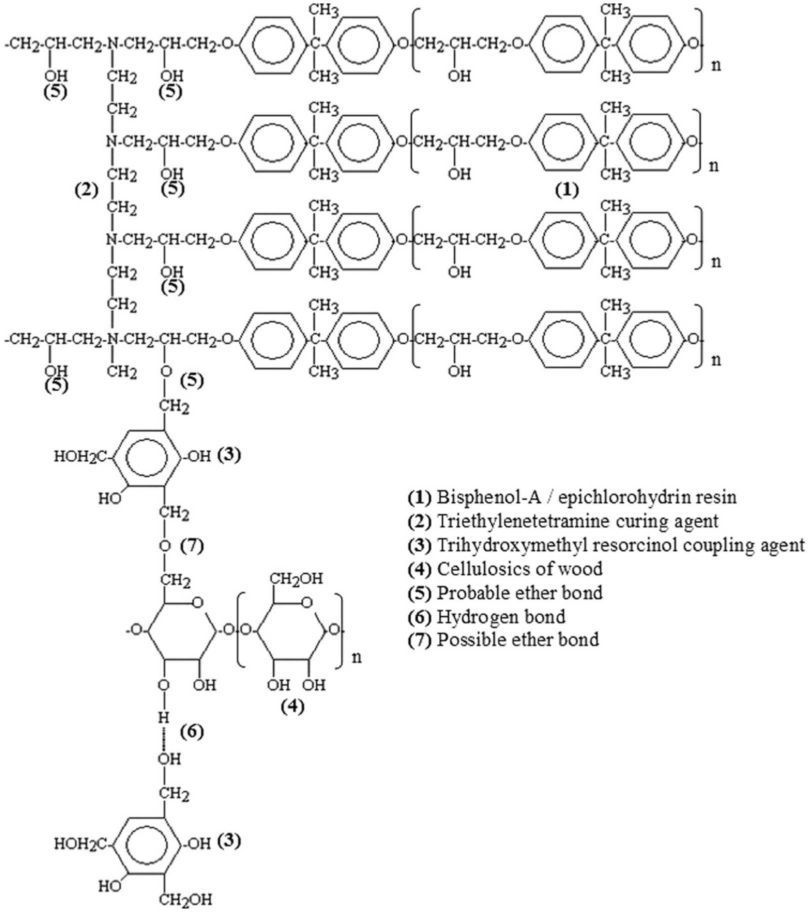

FIGURE 4 First mechanism proposed by Vick *et al.* (1995) [33] for covalent and hydrogen bonding of hydroxymethylated resorcinol adhesion promoter to the BPA epoxy adhesive and cellulosic components of wood.

ether linkages with the primary hydroxyl groups on cellulose of wood, as shown at position (7). In this way, a completely cross-linked polymeric network could be formed between the epoxy resin and the cellulosics of the wood, through the chemical linkages of the HMR adhesion promoter. If conditions and cellulosic structures were not available for covalent bonding, then hydrogen bonding could also take place, as shown in Figure 4 at position (6). When cell walls are thoroughly covered by a multi-molecular layer of highly reactive HMR of relatively small molecular size, opportunities would abound for high-density hydrogen bonding with primary and secondary hydroxyls of wood lignocellulosic components.

Gardner and Tze (2001) [45] examined the adhesive wettability of wood treated with HMR and characterized its surface free energy, to determine if bond enhancement could be attributed to adhesive wettability and whether the proposed adhesive bonding mechanism was correlated to changes in wood surface free energy resulting from the HMR treatment. Adhesive wettability was determined by measuring contact angle changes as a function of time for PF and pMDI on Southern pine and Douglas fir treated with HMR. The surface free energy was determined from the contact angle data of four probe liquids: water, formamide, ethylene glycol, and methylene-iodide. The results showed that the HMR treatment increased the contact angle formed by the adhesive on the timber surface and decreased the rate of adhesive wettability of wood, this effect being more pronounced for Southern pine wood. The surface characterization indicated that the treatment reduced the dispersive component and increased the polar component of the surface free energy. Gardner found that the decreased wettability was correlated with the dispersive component that decreased also with the treatment. These results implied that the bond enhancement could not be attributed to improved adhesive wettability, and the increase in the polar component (possibly due to the presence of hydroxymethyl groups on the wood surface) promoted the formation of covalent bonds and strong secondary bonding interactions between the HMR-treated surface and the adhesive. Gardner's findings seemed to agree with the mechanism proposed by Vick *et al.* (1995) [36].

The fact that the formation of ether bonds is usually done in solution under acidic conditions (wood is usually slightly acidic but the HMR is slightly alkaline) and the notion that epoxies do not react with alcohols at room temperature originated doubts concerning the hypothesized mechanism where covalent chemical bonds would be formed between the adhesive and HMR, and possibly between HMR and wood. Having this in mind, Christiansen (2005) [46] conducted a study in order to test the mechanism proposed by Vick *et al.* (1995) [36]. Two sets of experiments were developed. The first set of experiments involved the modification of the mechanical integrity of the HMR to decrease its strength and stiffness. This was achieved by displacing some resorcinol (which can crosslink into a three-dimensional network) by 2-methylresorcinol (which cannot crosslink) at various levels to decrease the maximum possible crosslink density of HMR, but retain hydroxymethyl groups on the active primer for reaction with the adhesive and possibly with wood. The second set of experiments involved the evaluation of the ability of the novolak-based HMR (n-HMR) to develop chemical covalent bonds with the epoxy adhesive. HMR-primed Southern yellow pine was stored at high temperatures and/or long times (23°C for 3 months; 50°C for 4 days; and 70°C for 24 hours) before being bonded with the FPL 1A epoxy adhesive. The rigorous storage conditions should allow any remaining hydroxymethyl groups in the HMR primer to react and be consumed, thus not leaving any reactive hydroxymethyl sites that would be able to chemically react with the adhesive. The results from the former set of experiments showed a pronounced reduction of the ability of the wood-adhesive bond to resist cyclic swelling and shrinking cycles and comply with the 5% maximum delamination limit for softwoods set by ASTM D 2559 [47]. In the second set of experiments, the storage of the primed wood surface at severe conditions did not appear to affect the durability enhancing properties of the HMR primer and the HMR primed wood maintained an excellent bondability even after 3 months of storage, without the need for re-planing the wood surface. The results obtained by Christiansen seem to indicate that the mechanism of bond durability enhancement by the HMR primer is achieved by mechanical stabilization of the wood surface, instead of through chemical reactions with the adhesive. This conclusion is in line with the findings of Son and Gardner (2004) [48] who found that the HMR treatment improved the dimensional stability of wood, since there was a reduced swelling of HMR-treated samples compared with the untreated samples in a water-immersion test. The fact that the HMR does not lead to bond stabilization through the formation of covalent bonds makes it an adhesion promoter, and it should not be classified as coupling agent.

Findings from more recent studies (Son *et al.* 2005, Tze *et al.* 2006, Sun and Frazier 2005) [49–51] regarding the characteristics of the HMR-treated wood adhesive bond continue to support the theory that the likely mechanism of bond durability enhancement by the HMR primer is via dimensional stabilization of the wood surface. It is postulated that HMR will penetrate the wood cell wall on the molecular level forming an interpenetrating polymer network, which will impart dimensional stability to the wood surface, but at the same time it will decrease the glass-transition temperature of lignin, and to a lesser extent, of hemicellulose, thus acting as a plasticizer, creating a more flexible interphase between the adhesive and adherend, ultimately delaying the damages induced by hygrothermal stresses in weathering.

Research at the Forest Products Laboratory [34,36,38,46] demonstrated that when HMR is used to prime wood surfaces before bonding, there is an increase in delamination resistance, shear strength, wood failure, and deformation resistance. The HMR enables BPA epoxy adhesives to develop bonds of extraordinary structural durability to two softwoods (Sitka spruce and Douglas-fir) and two hardwoods (yellow poplar and yellow birch) that meet the delamination requirements of ASTM D2559. Also, when the same epoxy adhesives were used to laminate vinyl ester and phenolic fibre-reinforced plastics to HMR primed lumber, the composites were extraordinarily resistant to delamination. Moreover, the HMR also improved adhesion of one-part polyurethane adhesive on yellow birch and Douglas fir, which allowed the bonds to meet the strength and durability requirements of ASTM D2559. When chromated copper arsenate (CCA) treated Southern pine laminates were bonded with epoxy, phenol-resorcinol, EPI, and pMDI, the bonds also met the delamination requirements of ASTM D2559.

So far, two types of HMR have been evaluated in laboratory studies: the original version of HMR used by Vick (1995) [35] and a new novolak-based HMR by Christiansen *et al.* (2000) [52]. The former HMR has three main disadvantages that make its commercial use difficult. First, the original HMR has no storage life, thus, every batch has to be mixed on site from accurately measured proportions of the starting chemicals, which is time consuming and prone to error. The second disadvantage is that there is a 3 to 4 hour waiting period before the adhesion promoter can be used, and after that only 3 to 4 hours of working life remains. The third obstacle is the 18 to 24 hours drying time at ambient temperature required for the HMR-treated wood surface before adhesive application, which is due to the amount of water contained in the HMR solution (95%). During drying, water evaporates from the wood surface while the resorcinol and formaldehyde react.

In order to solve the previous obstacles, Christiansen *et al.* [42,43,52–54] developed a novolak-based HMR (n-HMR) adhesion promoter that allows partial reaction and then it has unlimited shelf life. The adhesion promoter has two chemical states and the mixing procedure is divided into two steps. The first mixing step provides an n-HMR solution. In the second step, the adhesion promoter is modified from the novolak status to the activated status by the addition of formaldehyde. The n-HMR from the first mixing step can be stored at ambient conditions for at least 3 days, but no longer than 6 days. Once activated, the adhesion promoter can be applied either immediately or within about 7 hours of activation, although the best result is obtained after 1 hour of activation at ambient temperature. The n-HMR adhesion promoter is as effective as the one-step HMR in providing exterior durable bonds of epoxy adhesive to Douglas-fir laminates. Once primed with the n-HMR, the wood forms strong bonds even if bonded 2 weeks later [53,54]. Eisenheld and Gardner (2005) [55] conducted an experiment in order to reduce the processing time of an n-HMR adhesion promoter from 24 hours to less than 30 minutes by applying an infrared heating drying step. For this experiment, the n-HMR adhesion promoter was used at 5 and 10% solids content. Shear tests were conducted on hard maple (*Acer saccharum*) bonded with the FPL-1 epoxy adhesive. The best bonding performance was obtained at an n-HMR drying time between 15 and 20 minutes. The dry shear tests of the bonds produced with n-HMR dried for 24 hours at ambient temperature and the n-HMR dried for 15–20 minutes with infrared light (60–65°C), with n-HMR of 5 and 10% solids content, had similar results, all of them giving a shear strength of 20MPa. Regarding the wet shear tests, only the laminates dried with infrared light met the 6 MPa minimum standard for structural adhesives (ASTM D2559-04), obtaining shear strengths between 8 and 10 MPa. In this study it was also concluded that the n-HMR spread rate (146 and 220 g/m^2) and the n-HMR solids content did not significantly affect the bond performance. Nevertheless, Eisenheld recommends using the lower spread rate of 146 g/m^2, because of the higher amount of water within the n-HMR solution; if less water is applied to the wood surface, less heat is required to dry the n-HMR solution. He also recommends the use of an n-HMR solids content of 5%. This last development of a modified HMR makes the adhesion promoter more user-friendly and makes viable the industrial production of bonded structural components.

3.3. Other Adhesion Promoters

Several other adhesion promoters and coupling agents exist, but, unfortunately, the majority of the reported studies refer only to their application in non-cellulosic substrates. However, preliminary work by

Frihart and Chandlen (2006) [56] at the Forest Products Laboratory evaluated melamine-based primers to enhance epoxy bond durability. The idea of undergoing this experiment arose from the fact that melamine-formaldehyde adhesives form bonds with good weather exposure durability, since some of their chemicals reduce wood swelling, enter into wood cell walls, and strengthen them. In addition, melamine is more easily studied (due of its significant nitrogen content, when compared with the lack of nitrogen in wood components) than the HMR primer. The HMR study is limited by its similarity to wood lignin. Frihart studied two primers, a catalysed melamine-urea-formaldehyde and a catalyzed hexamethylol melamine methyl ether primer. The second primer was used because previous studies [57] showed that methoxymethyl melamine reacts covalently with hydroxyl groups in wood, forming a hardened network, which leads to an increase in bulk Brinell hardness and a decrease in swelling for the treated European beech sapwood. The effects of the melamine-based primers were evaluated using dry and wet compressive lap shear tests. The timber used was yellow poplar (*Liriodendron tulipifera* L.) sapwood and the adhesive was the FPL 1 A. The shear tests results showed that both primers improved the durability of the epoxy adhesive bonds on yellow poplar. However, further studies are necessary to obtain additional information about the mechanism of this enhanced wood bond durability under wet conditions, as well as to confirm its ability to work with other timbers and adhesives.

4. COMBINED TREATMENTS

Successful adhesion between non-bondable or hard-to-bond materials can also be achieved through the combinations of the aforementioned physical and chemical treatment methods. The most common example is in the enhancement of the mechanical properties of composites, where good adhesion between the reinforcing agent and matrix must exist.

Gramlich *et al.* [58] conducted a study where physical and chemical treatments were used to improve the adhesive bonding between wood–plastic composites (WPC) formulated with polypropylene and a commercial 2-component epoxy adhesive. The treatments were performed on planed extruded WPC and consisted of chromic acid treatment, flame treatment, water treatment, flame followed by water treatment, and water followed by flame treatment. The chromic acid and flame treatments increased the average shear strengths by 97 and 67% compared with the untreated samples. The water treatment resulted in an increase in shear strength of 31% relative to the control. The combination of flame and water treatments showed increased shear strength relative to the individual treatments alone, indicating that the two processes might act synergistically to facilitate the formation of stronger adhesive bonds.

Another example of the successful use of combined surface treatment methods is given by Gutowski, of CSIRO Polymer Surface Engineering Group in Melbourne, who has patented a SIlane on CORona process (SICOR bonding technology) which enables the successful adhesion of paints, adhesives, inks, metallic coatings, and other materials to otherwise non-bondable or difficult-to-bond materials (*e.g.* polyolefins) without resorting to hazardous chlorinated solvents or chlorinated primer ingredients. In the SICOR process, the untreated substrate is first oxidized using either a flame or a coronal discharge process and then coated with a hydrolyzed silane, which provides a molecular "bridge" between the oxidized polymer surface and the material bonded to that surface. Until the development of the SICOR bonding technology, silanes and other organofunctional adhesion promoters were effective for promoting adhesion only on the surfaces of metals and ceramics [59–63].

Approaches similar to those used in enhancing adhesion of synthetic polymers could be used whenever improved adhesion and durability of adhesives, coatings, and other materials to timber is needed. However, studies addressing the feasibility of applying this technology and the combination of other treatments/primers to solid timber adherends are still missing. To address this situation a study is being developed by the authors at Oxford Brookes University regarding the durability enhancement of epoxy bonded timber structural joints involving European softwood and hardwoods [14,15]. Gutowski is also conducting experiments at CSIRO addressing the adhesion enhancement of bonded joints prepared with structural grade 1K-polyurethane adhesive and Australian hardwoods [61,64].

5. CONCLUSIONS

With the development of adhesion science and technology, it has become relatively straightforward to produce adhesive bonds of very good durability. However, in certain applications where adhesives like epoxies and polyurethanes are needed, the joints produced do not have adequate exterior durability. In these situations it becomes necessary to use surface treatments, adhesion promoters, or coupling agents to improve bond strength and durability.

5.1. Surface Treatments

Corona and flame treatments are considered to have a low environmental impact, and they have an important role as a replacement for chemical pre-treatments.

Corona treatment holds much promise, but the literature has focused on a limited number of adhesives (UF, PRF, PVAc) and timber species (apitong, Japanese cypress, Japanese beech, teak, birch, pine, isunoki, purple heart, oak, spruce, beech, robinia). Besides that, the aforementioned authors' conclusions are based mainly on wettability tests (made with only one or two different probe liquids), and not on mechanical testing of bonded joints, which may lead to different results. Therefore, more investigation is necessary to correlate the wettability enhancement (with at least three or five different probe liquids) with the strength and durability improvements in adhesively bonded joints. Also, more adhesives and timber species should be considered. Finally, in industrial terms, when considering corona treatment, companies will be forced to make provisions to deal with the ozone problem. The main advantages of this technique are that the treatment is less species specific and less susceptible to variation than flame treatment, and it can be applied to surfaces that are not flat.

The effects of flame treatment tend to be species-specific and more susceptible to variation. Also, there have been fewer research studies involving this technique applied to timber, compared with corona. In addition, they focus on a limited number of adhesives (PVAc) and timbers (teak, pine, birch, oak, meranti, western hemlock, beech, Douglas fir, iroko, spruce). Again, the authors' conclusions are based mainly on wettability tests (made with only one or two different probe liquids), and not on mechanical testing of bonded joints. Therefore, more fundamental research is needed to overcome this situation and to allow the use of this technique at an industrial scale. Nevertheless, the flame treatment has two mains advantages in relation to the corona: there is no substrate thicknesses restraint and no ozone is produced during the treatment.

5.2. Adhesion Promoters

Silanes show much promise, but there is a need to achieve a molecular understanding of the complex interplay of factors that determine silane adsorption or adhesion to timber substrates. Also, failure to understand the experimental parameters for each type of organosilane/adherend system could prevent improvements in adhesive joint durability and, thus, provide a misleading and false notion of the beneficial qualities of silane coupling agents. Therefore, the optimum application conditions for each silane/adhesive/timber combination must be determined prior to any attempt at commercial utilization.

Hydroxymethylated resorcinol has been used successfully with Sitka-spruce, Douglas-fir, yellow poplar, yellow birch, and Southern yellow pine. HMR surface treatment has increased the adhesion of epoxy, EPI, pMDI, and PRF resin to wood. In addition, for bonding wood to fibre-reinforced polymers, HMR promotes the exterior durability of the joints bonded with adhesives, such as epoxy, PRF, and vinyl ester. Consequently, this technique seems ready for industrial application, at least for those timber species and adhesives. Nevertheless, studies to clarify some aspects of its action mechanism are still needed.

Melamine-based primers constitute another group of potential adhesion promoters which can give good results in improving timber bond durability, but very little research has been done so far. Thus, further studies are necessary to obtain additional information about this group of adhesion promoters.

5.3. Combined Treatments

It seems likely that an optimum combination of treatment and adhesion promotion exists, for different species and adhesive systems. The synergistic effects are very real for the investigations undertaken so far but, due to the limited research conducted until now on cellulosic adherends, more research is needed to overcome this situation and to allow the use of optimized techniques at a commercial level.

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