EFFECTS OF WOOD PRESERVATIVES IN ADHESIVE CURING AND CHANGES IN SURFACE CHARACTERISTICS OF TREATED WOOD

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ABSTRACT

The effects of various wood preservative systems and treatment processes on mechanical and physical properties of wood material have been well documented. Particularly, bondability and wettability properties of wood surfaces are directly affected from surface energy and roughness. In this article, changes of surface energy components of preservative treated wood surfaces have been investigated. Preservative chemicals play important role on post-treatment surface energy values which depend on wood species, preservative type and retention value. The effects of wood preservative chemical presence on curing studies are also discussed through the Differential scanning calorimeter (DSC) and Infrared spectrometer (IR) techniques. Current literature was scanned for compatible adhesive preservative combinations. The compatibility was examined under the cyclic delamination tests for various adhesive systems against wood preservatives commonly in use. In addition, the development processes of some coupling agents to improve bondability of preservative treated wood were discussed. Furthermore, long-term durability issues of preservative treated and bonded glue lines were evaluated through changes in moisture content, alteration of pH and inhibition of condensation reaction. Finally, the surface energy values of some wood species treated with common wood preservative chemicals are also listed. The information may be useful to solve problems in treated wood bonding area as well as developing new chemical adhesive formulations for chemically and physically modified wood surfaces.

SURFACE CHARACTERIZATION

Surface characterization area evaluates contact angles, surface energies and surface topography of adherents to determine the wettability and bondability of different surfaces. Contact angle reflects the physical and chemical affinity between a surface and a liquid such as adhesive. As a result, contact angle analysis has been used to characterize the wettability of a wood surface and then to predict its adhesion performance by many researchers.

Maldas and Kamden (1988 a, b) have reported some considerable changes on Chromated copper arsenate (CCA) treated red maple surface as follows;

a) wood cell walls are covered with 1-5µm solid deposits, which are rich in chromium, copper and arsenic.
b) Oxygen/Carbon (O/C) ratio of CCA treated samples is increased due to the added oxygen atoms from the CCA on the surface, and at the same time reduced presence of carbon or C1.
c) The surface pH of untreated wood was 6.6 (± 0.13) as opposed to 5.9 (± 0.17) for CCA treated wood.
d) The surface roughness profiles for CCA treated wood changed considerably compared with those of untreated wood. (Average roughness for water treated wood is 1.72, for CCA treated wood 2.48)
e) For all probe liquids, the contact angles for CCA treated wood are higher, which indicates poor wettability when compared with untreated wood.
f) According to the time dependent contact angles, which is considered a good indication of the efficiency of the penetration of the liquid into the wood, the penetration of water into the untreated wood was faster than with CCA treated wood. This indicates that the CCA treated surface is hydrophobic.

In summary, they concluded that the CCA treated wood became rougher, hydrophobic, and acidic due to deposition of As, Cu, Cr oxides on the wood cell wall. The C1, C2, and C3 contents and the O/C ratio also changed upon CCA treatment and the surface became oxygen rich. Time dependent (dynamic contact) contact angle measurements on CCA treated wood surface with water, glycerol, and phenol formaldehyde (PF) resin showed poor wettability and low liquid penetration.

In contrary, another similar study on artificially weathered CCA treated southern pine by Zhang et al. (1997) highlighted that the CCA treatment results in improved resorcinol formaldehyde (RF) resin wettability, as expressed by lower contact angle of RF on the CCA treated than on the untreated southern pine surface. Total surface tension of the CCA treated wood is higher than the untreated southern pine. Interestingly, they also noted that the total surface tension of both the CCA-treated and untreated southern pine increased as a result of the exposure to accelerated-weathering cycles which cause surface oxidation.

According to Zhang et al. (1997) CCA treated wood has been shown to be coated with deposits of metallic oxides causing a microscopically rough surface. This roughness, coupled with some polar affinity of oxides with RF resin, may trigger wetting of CCA surfaces beyond that found on untreated wood surfaces. Wax content of commercial CCA treatments is used to explain the higher water contact angle for CCA treated wood. This showed that CCA treatment influences the water repellency more than the adhesive wettability of the wood.

In terms of evaluation of bond strength, they reported approximately 20 percent shear strength loss (statistically significant) as a result of the CCA treatment (at 0 aging cycles). Wood failure percentage (WFP), however, did not show any significant difference. The accelerated-weathering cycles examined in their study did not greatly reduce the bonding properties of the CCA treated southern pine. Finally, they concluded that aged CCA treated southern pine should have reasonable bonding properties with a proper adhesive and adequate bonding technology (Zhang et al. 1997).

Shaler et al. (1988) reported that with application of manufacturers pressing conditions, resin systems, and preservative retention level in their experiment, the performance of CCA treated laminates met the American Institute of Timber Construction (AITC) requirements for glue line performance in shear strength and cyclic delamination. The mean percentage wood failure of CCA/CCA joints, however, failed to meet the required 70 percent value. (Shaler et al. 1988)

In a Scanning Electron Microscopy (SEM) work, Vick and Kuster (1992) found that the lumen surfaces are completely covered by heavy concentration of hemispherically shaped deposits ranging in diameter from around 1.0 μm to essentially invisible at a magnification of 5000x. Theoretically this causes very little opportunity existed for the adhesive to make molecular-level contact with lignocellulosic constituents of cell walls without physical blocking by the chemical deposition. As the acidic CCA preservatives contact the wood, the pH increases instantaneously as ion-exchange and adsorption reactions occur between the metals and the wood. In comparison with one-and two component preservatives that had no marked effect on decrease of aromatic or carbonyl groups, all three components of CCA apparently were required for reactions to take place with these groups. Since phenolic resins are rich with polar hydroxyl groups that can form hydrogen bonds with polar functional on lignocellulosic constituents in cell walls. But in case of treated wood, as they proposed, the insoluble CCA metal oxides already occupied these functional sites which might have been available for hydrogen or perhaps covalent bonding. Despite the presence of insoluble deposits blocking contact between adhesive and wood, they concluded that mechanical interlocking by a deeply penetrating phenolic adhesive can produce delamination-free bonds to CCA-treated southern pine even after severe cyclic aging tests. (Vick and Kuster 1992)

Resin Curing Studies in The Presence of Wood Preservatives Using Differential Scanning Calorimetry (DSC) and Infrared Spectrometer (IR)

Vick and Christiansen (1993) offered Differential Scanning Calorimeter (DSC) thermograms indicating that a solution of CCA preservative caused a strong exothermic reaction with phenol-formaldehyde adhesive in which a portion of the adhesive reacted at lower than normal temperatures. Individual metallic ions of Cr (VI), Cr (III), Cu (II) and As (V) in solutions of model compounds also reacted with the adhesive, but only Cr (VI) reacted in the same low temperature range as the solution of CCA preservative. However, when the CCA preservative was chemically "fixed" within the wood no accelerated reactions of the adhesive were evident. (Vick and Christiansen 1993)

In an Infrared Spectroscopy study of phenol resorcinol formaldehyde (PRF) resin cure, Miyazaki et al. (1999) agreed that the treatment with alkyl ammonium compound (AAC), ammoniacal copper quat (ACQ), and copper azole (CA) does not inhibit the curing of PRF. The addition of preservatives did not have any effect on the absorption strength at 1140 cm^{-1}, 1040 cm^{-1}, and 970 cm^{-1} of infrared spectrum, which are characteristic bands for the curing of PRF. According to their increased relative rigidity and decreased tan δ for the Torsional Braid Analysis (TBA) measurements, however, it was concluded that the addition of preservatives accelerated the cure of PRF. (Miyazaki et. al. 1999).

Cameron and Pizzi (1985) reported that the shear is unaffected by increasing levels of CCA retention, although the percentage wood failure is decreased. They recommended that the PRF resin is suitable for use at all levels of CCA retention were tested (16, 20, 32 kg/m^{3}, respectively). Interestingly, they recorded higher strength results with 32 kg/m^{3} retention and 200g/m^{2} adhesive spread rate. This is tried to be explained by the fixed chromium on wood surface. Chromium forms a strong, stable and irreversible complex with phenolic resin, resulting in higher surface wetting. (Cameron and Pizzi 1985).

Compatible Adhesive-Preservative Systems

Winandy and River have recommended phenol-resorcinol and pentachlorophenol (penta) as a compatible adhesive-preservative system and phenol-resorcinol and CCA (cured at ambient

temperature) as an incompatible system based on their preliminary evaluation for the proposed test method of adhesive-preservative compatibility. It was claimed that although early indications showed promising results of CCA-phenol-resorcinol compatibility, industrial experiences and laboratory studies seem to indicate otherwise and some mixed results. (Winandy and River 1986). They concluded that their proposed vacuum-pressure soak-dry (VPSD) shear test with evaluations of shear strength and wood failure characteristics after multiple VPSD cycles is an effective and more informative test than the standard cyclic delamination test method.

Vick et al. have worked the compatibility of non-acidic waterborne preservatives (such as didecyldimethylamonium chloride (DDAC), DDAC with copper, DDAC with carbamate, sodium fluoride and ammonium hydrogen difluoride) with phenol formaldehyde adhesive. They reported that all these non-acidic waterborne preservatives mentioned above did not interfere with the adhesion of PF adhesive to aspen veneers treated at retentions of 0.2, 0.4, and 0.6 pcf level.

Ammoniacal copper zinc arsenate (ACZA) did not interfere with adhesion at lower retention but at higher retention levels, bond integrity fell below standards (Vick et al. 1990).

Sellers and Miller summarized that an expensive, straight RF adhesive may bond CCA-treated lumber satisfactorily for exterior exposure glulam products. They also reported the success of the emulsion-isocyanate adhesive in dry block shear test, but this adhesive failed in the standard delamination test. (Sellers and Miller, 1997)

In general, there is limited information with water-borne preservatives and lack of data in oil-borne preservatives-adhesives compatibility issues in the literature.

Trials to Improve Adhesion of Treated Wood

Vick (1990) has pioneered in this area and he successfully patented his hydroxymethylated resorcinol coupling agent (HMR) in August 6, 1996. Coupling agents are chemical molecules with dual functionality. In use, one part of the molecule will adhere to one surface (e.g. wood surface) while another part of the molecule will adhere to the surface of another material. (e. g. an adhesive polymer). He reports that when CCA-treated southern pine laminates were primed HMR and bonded with epoxy, phenol-resorcinol, emulsion polymer/isocyanate, and polymeric diisocyanate adhesives, the bonds met the delamination requirements of American Society for Testing and Materials (ASTM) D-2559. (Vick 1995). He also studied the effects of HMR coupling agent with PRF, melamine urea and melamine adhesives on CCA-treated southern pine lumber. All in these test, HMR coupling agent greatly enhanced the durability of adhesion in southern pine lumber laminates treated with CCA preservatives to retention levels of 0.4 and 0.6 pcf. The PRF adhesive met the 5% maximum delamination requirement of ASTM D-2599. (Vick 1995 and 1997) In his theory, the mechanism by which the HMR coupling agent bonds to CCA treated wood is somewhat different from bonding to untreated wood. "It appears that because of relatively small molecular size of the monomeric hydroxymethylated resorcinol species and their highly polar nature, the species physicochemically adsorb and mechanically interlock within the microstructure of metallic oxides. Therefore, the metallic oxide surface is converted to highly polar and reactive surface by depositing the multi molecular layers of the HMR coupling agent." he says.

Effects of Wood Preservative Treatment on Glue Line Performance

Different researchers with different approaches have reported some contradictory results on this area in the literature. A recent work by Kilmer et al. (1998) reported some important points of bondability of four hard wood species after being treated with creosote (pre-treatment).

They utilized five hard wood species and five different adhesive systems in two exposure levels as ambient and vacuum/pressure/soak (VPS). Although the elevated temperature cured PRF resin system produced the highest and most consistent glueline shear strength and percent wood failure values, they did not recommend any of these resin systems as suitable adhesives for use in bonding creosote treated hardwood for structural applications. They highlighted that the EPI systems (consists of a reactive emulsion polymer mixed with an isocyanate cross-linker) produced some of the lowest average percent wood failure performance values under VPS exposure level. According to Kilmer et al. (1998), poor bonding was attributed to a combination of improper wetting and of the wood surfaces as well as inhibition of moisture absorption from the glue film by the creosote thus delaying, or preventing proper cure. They used a two step surface preparation for creosote treated billets:

1) Steam cleaning; in a stainless steel vessel exposing to 115° C saturated steam at atmospheric pressure for one hour followed by a 50.7 kPa Hg vacuum for 30 min.

2) Surface planing; 1.6 mm surface planing immediately prior to layup. (Kilmer et al. 1998)

Similar glue line shear strengths were reported by elevated-temperature cured PRF relative to the room temperature cured PRF and RF adhesive formulations by Janowiak et al. in another study (Janowiak et al. 1992). The necessity of higher curing temperatures may indicate that the curing of the adhesive systems is somewhat slowed down by the presence of preservative. They observed that the major limitation for lamination of hardwoods was not adequate shear strength but rather the magnitudes of observed percent wood failure. Preservative treatment with CCA was not found to be an adverse factor in bonding different wood species, while oil-borne penta was observed with statistically significant lower glue line properties derived from several species-adhesive combinations used in their experiment. (Janowiak et al. 1992).

According to Raknes, the presence of a preservative in the wood can influence the formation of adhesive bond one of following ways;

a) by causing too high moisture content in the wood
b) by altering the pH of the adhesive
c) by inhibiting the condensation reaction
d) by delaying water removal from the glue line
e) by preventing the adhesive from wetting the wood surface

It was concluded that CCA treated beech wood may be satisfactorily bonded with RF and PRF type adhesive systems, even at fairly high preservative concentrations. (Raknes 1963). He also reported that the preservatives used seem in many cases to delay hardening of the adhesive systems, but this can be corrected with application of suitable adhesion conditions. Considerable differences were mentioned between the preservatives while the preservative concentration showed little impact on adhesion properties in this particular experiment. (Raknes 1963).

Selbo reports in his "Long Term Effect of Preservatives on Gluelines in Laminated Beams" titled work that adhesive joints in laminated beams made with resorcinol, phenol resorcinol, and melamine-resin glues and post-treated with several preservatives are not harmed by treatment with commonly used wood preservatives. (Selbo 1959 and 1967). He recorded several decreased values in shear strength ranging from 2% to 21% depending on the adhesive systems, wood species and type of preservative. He also concluded that no significant difference in the performance of three types of glues (resorcinol, phenol resorcinol and melamine) and creosote provided excellent protection against checking of laminated beams exposed to the weather for two decades.

CONCLUSIONS AND RECOMMENDATIONS

Recent research in surface characterization of treated wood reported that there are changes on surface properties, such as, preservative accumulation on cell lumens, surface energy and wettability, C/O ratio, surface hydrophobicity and roughness. There are SEM micrographs which visually proof the physical accumulations of metallic preservative salts on lumen surface. The author highlights some contrary data on this area and necessity of additional research to clarify this as well as a definite need of work especially on surface characterization of oil-borne preservative treated wood. The different results between the two major studies by Maldas and Kamden (1998) might be raised the artificial weathering effect in the second research. Maldas et al. have utilized unweathered red maple samples while Zhang et al. (1997) have worked with artificially weathered CCA-treated and untreated southern pine. Therefore, preservative/pressure treatment should be taken into account in wetting and bondability studies of treated wood.

Differential Scanning Calorimetry (DSC) and Infrared Spectrometry (IR) are very useful tools for determining resin cure under the influence of different chemical such as various wood preservatives. But some future work needed in this are, in terms of simulating the „real life" existence of wood preservatives in treated wood. Especially, there is almost no study on the effects of oil-borne preservatives in resin cure in the literature.

A future work for compatibility of preservative-adhesive systems with utilizing improved standard tests which give more informative results than standard test also recommended.

Besides HMR, some different type of coupling agents including natural enzyme systems and free radicals might be point of interest to improve durability of treated wood bond lines as economical solutions in the near future.

Tab. 1: A comparison of total surface energy (γ ts) values (mJ/m^2) of some untreated and preservative treated wood species

Wood	Treatment	Retention (kg/m^3)	Total surface energy (mJ/m^2)	Reference
Red maple	untreated	-	47.65	Maldas and Kamden 1998
Red maple	CCA-C	n/r	52.96	Maldas and Kamden 1998
SYP*	untreated	-	36.61	Zhang et al. 1997
SYP	CCA-C	6.4	43.35	Zhang et al. 1997
SYP	untreated	-	42.16	Tascioglu et al. 2004
SYP	CCA-C	5.9	44.97	Tascioglu et al. 2004
SYP	CCA-C	66.6	47.94	Tascioglu et al. 2004
SYP	Cu-N**	0.97	41.19	Tascioglu et al. 2004
SYP	Cu-N	4.0	32.61	Tascioglu et al. 2004

*SYP : Southern yellow pine (*Pinus spp.*)
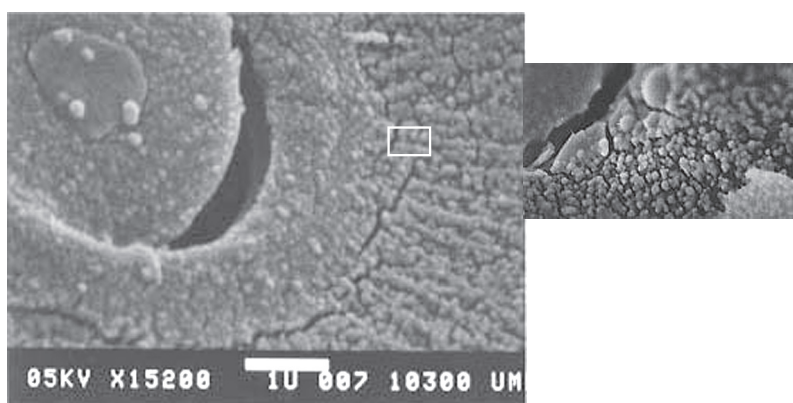
**Cu-N : copper naphthenate

Fig. 1: SEM micrograph of the surface of a cell lumen and ruptured torus from CCA pressure treated southern pine. Note that the lumen surface is completely covered with hemispherically shaped deposits of high surface energy metallic salts (chromium, copper and arsenic). The pit aperture shows the relative size of the metal deposits to the opening through which the preservative solution flowed. Also note the parallel alignment of metallic deposits to pit membrane's microfibril strands at the region of the margo (Magnification 15200x) (from Tascioglu et al. 2004)

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