Chemical Degradation of Treated Wood Based Composites

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Abstract

Wood based composites are treated with several chemical materials to protect from harmful effects of insects, fungi, moisture, fire and UV to provide long term service life. These chemicals affect wood and adhesives which are the main components of wood composites therefore modify physical and mevhanical properties . In this study, effects of acidic, basic and organic solvents on wood based composites were investigated.

Mechanical properties of wood composites treated with wood preservatives were reduced. This is releated with changes in wood/adhesive formation or wood/adhesive interfaces. Chemical type, reaction, treatment method, pH, retention, temperature and composite type in service are some of the major factors that play important role in chemical degradation of wood based composites.

Keywords: Chemical degradation, wood compozites, wood/adhesive interface

Emprenye Edilmiş Odun Kompozitlerinin Kimyasal Bozunmasi

Özet

Odun kompozitleri, böcek, mantar, rutubet, yangın ultraviyole vb. zararlı etkenlere karşı korumak ve böylelikle kullanım ömrünü uzatmak için çeşitli kimyasal maddeler ile muamele edilmektedir. Bu kimyasallar kompozit içerisinde ana bileşenlerden olan odun ve tutkal üzerinde çeşitli etkiler yaparak odun bazli kompozitin fiziksel ve mekanik özelliklerini etkilemektedir. Bu çalışmada odun ve tutkal üzerinde etkili olabilecek asidik, bazik ve petrol bazlı çözeltilerin meydana getirdiği etkiler incelenmiştir.

Ağaç malzeme koruyucuları ile muamele edilmiş odun kompozitlerinin mekanik özellikleri düşüktür, bu da odun/tutkal yapısında veya odun/tutkal ara yüzeyi arasında ki kimyasal değişimler ile ilgilidir. Kimyasalın tipi ve reaksiyonu, emprenye yöntemi, pH, retensiyon miktarı, kullanım alanındaki kompozit tipi, sıcaklık gibi etkenler odun kompozitlerinin kimyasal degredasyonunda önemli rol oynamaktadır.

Anahtar Kelimeler: Kimyasal bozunma, odun bazlı kompozitler, odun/tutkal arayüzeyi

1. Introduction

Since wood composites consist of two major components, wood and adhesive, the effects of chemicals solutions on wood composite materials can be

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grouped in as; 1)Effects of chemicals on wood, 2)Effects of chemicals on adhesives

With the increasing use of wood composite materials in a wide range of applications, their possible exposure to different chemicals has gained importance. The full understanding of chemical reactions and the compatibility of chemicals will provide useful information to the wood composite industry in terms of developing more durable products for specific end use. This paper covers basic chemical reactions of wood and adhesives with asidic, basic and organic solvents. Also, covered are examples of research common chemical treatments of wood composites and their effects on the physical and mechanical properties as well as durability performance.

2- Chemical attacks in wood

Wood is remarkably resistant to degradation when used in contact with chemicals. The effects of chemical solutions on mechanical properties depends on the chemical type. The hemicelluloses of wood appear to be most susceptible to attack by either acids or alkali. Studies indicate that about 70% of the variation in strength retention of wood treated with acid and alkali is associated with loss in hemiculluloses (Kass et al., 1970). Other effects of treatments that influence strength are acid-induced hydrolysis of cellulose and alkali-induced swelling. Resistance to acid attack is influenced by the degree of cellulose crystallinity, while low hemicellulose content in conifers increases resistance to both acids and alkali. Non-swelling liquids, such as petroleum oils and creosote, have no appreciable effect on wood properties. Wood properties are lowered in the presence of alcohol or other wood-swelling organic liquids even though these liquids do not chemically degrade the wood. Anhydrous ammonia markedly reduces the strength and stiffness of wood, but these properties are regained to a great extent when ammonia is removed.

In general, the following generalizations can be drawn from the literature; 1) Chemical solutions that decompose wood and wood composites by hydrolysis or oxidation have a permanent effect on strength, 2) Oxidizing acids such as nitric acid degrade wood more than non-oxidizing acids, 3)Hardwoods are more susceptible to attack by both acids and alkalis than softwoods because of their higher hemicellulose content, 4)Heartwood is less susceptible to attack by both acids and alkalis than sapwood (Goldstein, 1984).

Bublitz and Hull (1983) exposed solid Douglas-fir samples in several concentrations of hydrochloric acid over the period of one year. They reported that high temperature and acid concentration degrade Douglas-fir and length of exposure time is a factor. Work to rupture was reported the most sensitive property to degradation and MOE was the least sensitive. Even though hemicelluloses are most sensitive to acids, a major loss of cellulose was reported under the highest temperature and chemical concentrations. The acid first attacked the hemicellulose fraction of the wood, then the cellulose, and lastly the lignin.

2.1. Chemical reactions and damage mechanisms of wood in acidic medium

2.1.1. Acidic hydrolysis mechanisms of polysaccharides

The principal molecular mechanism of acidic hydrolysis proceeds in three steps; 1) proton of the catalyzing acid interacts rapidly with the glycosidic oxygen linking two sugar units, 2)forms a conjugate acid, 3) slow cleavage of the C-O bond yielding an intermediate cyclic carbonium cation.

Hydrolysis of glycosidic bonds usually follows a first order reaction. The most important and frequent hydrolytic reactions of cellulose and polyoses partly take place in a heterogeneous phase, with the polysaccharide component occuring in solid state in an acidic aqueous solution. If the sample to be hydrolyzed dissolved easily and totally in the acidic solution, both reaction partners are considered in a homogeneous phase.

Table 1: Factors influencing hydrolysis

Hydrolyzing Media	**Hydrolyzed Sample**
Kind of acid	Phase state (solid, liquid)
Concentration of acid	Molecular accessibility in the case of heterogeneous hydrolysis
pH value	Confirmation effects
Acid strength (pK_a)	Ring structure and substituents
Temperature and pressure	

2.1.2. Dehydration reactions of polysaccharides

Dehydration reactions are considered as side reactions of acidic hydrolysis conditions. The acid catalyzed dehydration under mild conditions leads to the formation of anhydro sugars with intra-molecular glycosidic linkages, resulting from the elimination as hydroxyl groups.

2.1.3. Oxidation reactions of polysaccharides

In principle, the hydroxyl groups of the sugar units and the reducing and groups of di-, oligo- or polysaccharides may be subject to oxidative attack. The converted groups are aldehyde, keto and carboxyl groups. The ring structure can be preserved or may be destroyed by cleavage of the ring oxygen bond and C-C bond. Important final degradation acids are uronic, aldonic, aldaric acids.

2.1.4. Reactions of lignin in acidic medium

Treatments of wood with concentrated mineral acids do not cause dissolution but condensation reactions of lignin, a fact is used in analytical lignin determinations. The main objective of sulfite pulping is the removal of lignin from wood to obtain a more or less delignified pulp. The reactions of lignin in pulping are limited to nucleophilic addition and displacement reactions. Under the acidic sulfite conditions the initial cleavage reaction at the C- α atom of phenolic and non-phenolic units is followed by the addition of a SO_3H group to the intermediary carbonium ion. This sulfonation of the benzylium ion increases the hydrophility of lignin, thus increasing the solubility in the aqueous liquor.

The initial step of lignin-removing bleaching reactions is generally an electrophilic attack on sites of high electron densities, followed by nucleophilic reactions.

2.2. Chemical reactions and damage mechanisms of wood in alkaline medium

2.2.1. Reactions of polysaccharides in alkaline medium

Initial reactions are solvation of hydroxyl ions causing a swollen state. At elevated temperatures the polysaccharides are attacked by strong alkali solutions, resulting in following important reactions; 1)dissolution of undegraded polysaccharides, 2)peeling of end-groups with formation of alkali-stable end-groups, 3)alkaline hydrolysis of glycosidic bonds and acetyl groups, 4) degradation and decomposition of dissolved polysaccharides, hydrolyzed fragments, and peeled monosaccharides.

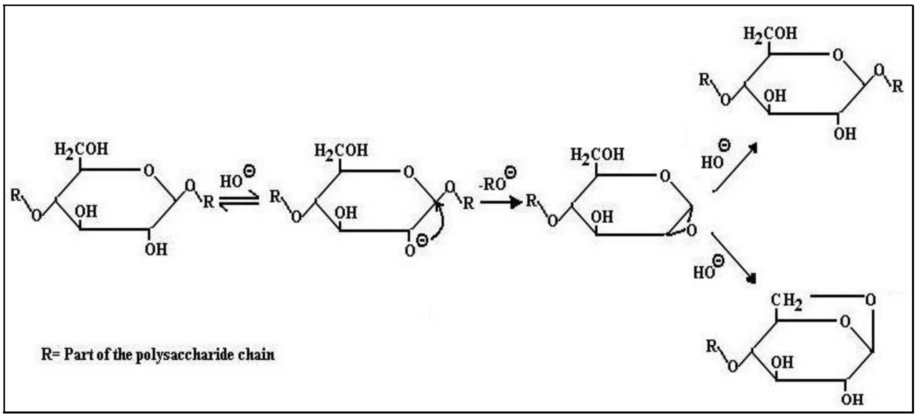

Figure 1. Hydrolsis of glycosidic bonds in alkaline medium

2.2.2. Oxidation reactions of polysaccharides

The most important reaction induced by oxygen radicals in the formation of carbonyl group at the C2-position of monomeric sugar unit, leading to a cleavage of the glycosidic bond by ß-alkoxy elimination.

2.2.3. Hydrogenation of polysaccharides

The principal reaction is a cataltic reduction in alkaline medium which yields sugar alkohols (polyos).

2.2.4. Reactions of lignin in alkaline medium

All types of aryl ether bonds of lignin are typically cleaved in alkaline medium, and also aryl-alkyl carbon carbon bonds are destroyed to some evtent.

2.3. Chemical reactions and damage mechanism in organic solvent medium

In the case of solvolysis with acid containing solvents in the presence or absence of water the cleavage of glycosidic linkages is mainly governed by the type of solvent. The non-aqueous solvents which are miscible with water (e.g. ethanol, dioxane) may act reaction partners. The addition of benzene is only used in pure alcoholic solutions, resulting in exclusively solvolytic reactions. Generally, solvolytic effects improve the cleavage rate of glycosidic bonds.

2.4. Effect of wood preservative chemicals on mechanical properties of solid wood

The current literature considers the effects of preservative treatment on mechanical properties of wood, especially waterborne preservative treatments. Some limitations and standarts have been released to control the preservative treatment effects on strength according to previous research. Oil-borne preservatives usually result in no appreciable strength loss because they do not react with cell-wall components. However, the termal effect with high pressures can adversely affect strength (Winandy 1991; Lebow, 1999).

Water-borne preservative treatments generally reduce the mechanical properties of wood. This reduction appears to be directly related to pre-treatment, treatment and post-treatment factors; such as retention, type of wood preservative chemicals, post-treatment drying temperature, incising etc (Winandy, 1995).

3. Chemical reactions of some major wood composite adhesives (PF, UF, MF and MDI) resins in asidic, alkaline and organic solvent medium

The permanence of a bond in wood composites may be affected by exposures to external chemical agents or by the latent chemical reactivity of the adhesive for an adherent. There is no one adhesive that is optimum for all chemical environments. As an example, maximum resistance to bases almost axiomatically means poor resistance to acids. Generally, adhesives which are most resistant to high temperature have the best resistance to chemicals and solvents (Landrock, 1985).

Several tests have been specified to evaluate bond strength on exposure to reagents such as acids, alkalies, water, sea water, petrol, organic solvent and lubricating oil (ASTM D 896-95: Standard test method for resistance of adhesives bonds to chemical reagents covers the testing of all types of adhesives for resistance to chemical reagents. The standard chemical reagents are those listed in ASTM D-543 and the standard oils and fuels are given in ASTM D-471).

Most organic adhesives tent to be susceptible to chemicals and solvents, especially at elevated temperatures. Some of the standard test fluids and immersion conditions (other than water, high humidity, and salt spray) are the following; 1) 7 days in JP-4 jet engine fuel, 2) 7 days in anti-icing fluid, 3) 7 days in hydraulic oil (MIL-H-5606), 4) 7 days in HC test fluid (70/30 v/v isooctane/toluene).

The temperature of the immersion medium is a significant factor in the aging properties of adhesives. As the temperature increases, more fluid is generally adsorbed by the adhesive and the degradation rate increases. In summary; 1)Chemical resistance tests are not uniform in concentrations, temperature, time or properties measured, 2)Generally, chlorinated solvents, such as dimethylformamide, dimethyl sulfoxide are severe environments, 3)Acetic acid is also considered a severe environment, 4)Amine curing agents for epoxies are poor in contact with oxidizing acids, 5)Anhydride curing agents are poor in contact with caustics

Table 2. Chemical Properties of Some Wood Composite Resins (adopted from ASM Engineering Materials, Bauccio, 1994.).

Chemical reagents at 25° C	**PF**	**UF**	**pMDI**
Nonoxidizing acids (20% H_2SO_4)	S	Q	S
Oxidizing acids (10% HNO_3)	Q	Q	Q
Aqueous salt solutions (NaCl)	S	S	S
Aqueous alkalis (NaOH)	Q	Q	Q
Polar solvents (C_2H_5OH)	S	Q	S
Non-polar solvents (C_6H_6)	S	S	S
Water (H_2O)	S	Q	S

(*) S= satisfactory, Q= questionable

Chemicals in the adherends, such as extractives or preservative/FRT salts, can migrate into adhesive line, which can destroy the adhesion in wood composites. Additionally, the by-products of an adhesive curing reaction may attack the adhesion line between the composite elements and cause loss of adhesion.

Pittman et al. examined the resistance of melamine treated southern yellow pine samples against some chemical warfare agents (HD=2,2'-dichlorodiethyl sulfide, VX= O-ethyl-S-[2-(N,N-diisopropylamino) ethyl] methyl phosphonothioate, TGD= methylphophonofluoric 1,2,2-trimethylpropylester). Melamine resin treated samples exhibited significant weight gains when they exposed to chemical warfare melamine resins to form some chemical bonds to the ray and cell lumens within wood via N-methylol condensation reactions.

Furthermore, cured melamine resins are highly crosslinked and not expected to swell in the presence of most chemicals. But the good adhesion to cell walls subjected the wood structure to increase stress as the volume contraction took place during curing. Since MF resins are rigid, brittle and highly crosslinked and have high Tg values, high internal stresses can develop and was not relieved by an elastic strain on the part of the resin. Thus, the wood deformed by forming checks and microcracks to relieve stresses. These microcracks take up chemical agents applied to the wood surfaces (Pittman et al., 1994).

4. Chemical treatment (wood Preservatives and FRT) and related property changes in wood composites

The wood preservative or/and fire retardant (FRT) treatment of wood-based composites can generally be performed in two ways. Chemicals can be applied before the boards are made by treating the veneers, flakes and particles. Or they can be added to the resin mix during composite manufacturing. The second way is the application of chemicals to the complete composite panels after manufacture, usually by a vacuum-pressure process.

Problems can arise when adding preservative and/or fire-retardant (FRT) chemicals to wood composites during manufacturing. The adverse effects of waterborne preservatives on the bonding of phenol-formaldehyde (PF) resins were reported by several researches as pH effects, incompatibility, between PF resins and preservatives, adverse effects on resin viscosity, decrease in the wettability of treated wood, reduction in the number of hydroxyl groups available for hydrogen bonding, and mechanical interference by preservatives salt with adhesion. Application of preservative and FRT chemicals during the manufacturing process of wood composites requires modifications in the production line resulting in high capital investment.

Difficulties are also encountered within treated boards after manufacture, such as reduction in mechanical properties, problems with over absorption and recovery of preservative solutions and swelling with aqueous systems.

The effects of preservative and/or FRT systems on both wood and adhesives as well as the interface between the matrix and wood elements should be investigated comprehensively.

Hashim et al (1994) tested several properties of medium density fiberboard (MDF), particleboard, and oriented strand board (OSB) treated with boric acid at two retention levels appropriate for protection against biological attack and fire. They reported that vapor boron treatment at wood-preserving and fire retarding levels has no statistically significant effect on mechanical properties (MOR, MOE and IB) on the wood composite types tested. The impact resistance of these composites was significantly reduced (25%-50%) depending on the board type and the retention level. This was explained by the cross-linking of borate ions with wood polymers turning the treated wood composite more glass-like (brittle) which resulting a reduction in impact resistance.

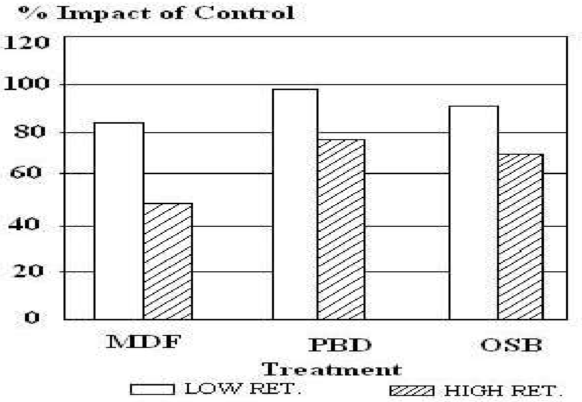

Figure 2. Impact strength reduction in borate treated wood composite boards (Hashim et al., 1994).

They also reported a 10 % reduction in internal bond (IB) strength for treated MDF boards at both retention levels. The particle geometry of the board, greater irreversible swell and water absorption of treated MDF during the water-soak tests were used to explained the phenomena. The effects of boric acid deposition on outer surfaces of individual fibers which reduce fiber/matrix interface bond may contribute to the reduction in IB strength and the increase to water absorption. Guyer and Hassfeld (1990) proposed that the reaction of trimethyl borate within composites is considered to occur primarily with the water molecules associated with the wood polymers and possibly with adhesive resins. Methanol, (a by product of this reaction), is also known to cause for swelling of wood polymers in a manner similar to water. The increased hygroscopicity of treated composite might be attributed to the penetration of methanol into the amorphous regions of the wood cell wall which forces the microfibrils apart. This swelling is considered a reversible phonomena due to the temporary presence of methanol. The irreversible swelling of the composite was believed to be caused by the presence of deposited boric acid and springback.

Kimmel et al (1994) tried to characterize the mechanical properties of creosote-treated LVL material. According to their results, LVL materials (red maple, southern pine and yellow poplar) were found to be uniformly treated with effective penetration using a modified pole treatment with clean creosote preservative. The LVL materials exhibited far different penetration characteristics in comparison to solid lumber. Creosote penetration was markedly enhanced, with improved uniformity in distribution of the preservative through treated section. This reduction in the preservative gradient (in comparison to solid wood) will ensure a more consistent treatment throughout the cross-section of larger structural members, aiding in protection against wood-decay fungi and insect attack. Higher creosote retentions were correlated with the lathe checks, which is more pronounced for the processed hardwoods than observed for southern pine. The relatively minor (in comparison to similar uptake of water) thickness swelling was related to spring-back of the desified veneers rather than directly related defect to the amount of creosote uptake. Thickness swelling for southern yellow pine LVL, for example, was recorded 85% greater than its solid lumber counterpart; however the creosote retention was nearly double for the LVL material.

Although the flatwise and edgewise flexural modulus indicated only minor reductions in stiffness of LVL material due to creosote treatment, the general trend was statistically insignificant. Both shear strength properties in parallel and perpendicular to glueline test orientations for treated versus control means were recorded similar, with no differences at the 95th percentile confidence level.

Another study by Lebow (1998) indicated that FRT treated plywood exhibited a rapid decrease in pH (especially formulations containing phosphoric acid). Addition of borate compounds (Timbor, disodium octaborate tetrahydrate) produced a measurable buffering effect whic slowed the decrease in pH. They reported strong relations between changes in pH of the FRT treated plywood and reductions in strength and energy related properties. They suggested that pH of the FRT plywood is a good indicator of its current condition and may have potential as a predictor of future strength loss as the plywood is subjected to elevated temperatures during service life.

Laks et al (1988) pointed out the compatibility of pMDI resin and borate in FRT treated flake board production. They examined that 5% borate

(TIMBOR) treated green flakes bonded together with powdered and liquid phenolic resins and an isocyanate adhesive. While phenolic bonded boards showed large reductions in internal bond (IB) and MOR, and a substantial increase in thickness swell (TS), with increasing borate content, the addition of borate to the pMDI bonded boards caused less bending strength loss and increase in TS and no effects on IB values. They postulated an explanation regarding the polarity of the phenolic adhesives. Borates can easily be dissolved in the very polar, water-containing glue line of the phenolics. The dissolved borate may interfere with the curing process through its buffering action on pH of the resin, therefore the cure rate. Since isocyanate resins are nonpolar and in soluble in water, the borate will not dissolve into the isocyanate glue line.

Solar radiation (UV) can cause chemical changes in molecular structure of wood preservative and/or FRT materials in wood composites. This change can result in some further chemical degradation and strength loss on wood components.

Copper compounds such as copper naphthenate (Cu-N) and copper carbonate catalyze the light induced degradation of cellulose under the solar radiation, resulting in strength loss. For this reason, careful choice must be made for copper compounds to be used in wood composites which will expose to sunlight. The degradation of the cellulose is probably also associated with a reaction between the copper and the substrate (Arsenault, 1973).

Penta also undergoes changes in sunlight. The degradation of penta in sunlight with release of HCI is well known. When water is present, penta will react under sunlight to form a variety of ethers, many of which apparently are more potent fungicides. Briefly, the activation or initiating reaction by solar radiation is the production of a pentachlorophenoxy radical and hydroxy radical. These react through intermediates to form compounds such as chloranilic acid, tetrachlororesorcinol, various ethers.

Phenols, cresols, and other aromatic compounds present in creosote and other organic solvents are also oxidized by sunlight (Arsenault 1973, Huber 1958)

5. Conclusions

The following conclusions can be drown from the above study; 1) Wood composites treated with wood preservatives and fire retardant treatments (FRT) exhibit reductions in mechanical properties (MOE, MOR, IB, impact strength, thickness swelling etc.), 2) These reductions are related to chemical changes in the wood/resin or wood resin interfaces, 3) Chemical type and reaction, treatment method, pH, retention, composite type in service temperature and RH are some of the major factors that play role in chemical degradation of wood composites, 4) More research is needed to explain the synergistic effect of variables mentioned above.

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