Kollman FFP and Cote WA (1968) *Principles of Wood Science and Technology*, vol. 1, *Solid Wood*. New York: Springer-Verlag.

Siau JF (1995) *Wood: Influence of Moisture on Physical Properties*. Blacksburg, VA: Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University.

Skaar C (1988) *Wood–Water Relations*. New York: Springer-Verlag.

Stamm AJ (1964) *Wood and Cellulose Science*. New York: Ronald Press.

Tsoumis GT (1991) *Science and Technology of Wood*. New York: Chapman & Hall.

US Department of Agriculture Forest Products Laboratory (1999) *Wood Handbook: Wood as an Engineering Material*. Madison, WI: Forest Products Society.

Chemical Properties of Wood

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Introduction

The chemical properties of wood are inextricably associated with and dependent upon its chemical composition. Fortunately, the major wood components are not numerous, and with only minor variations are found across all woody species. The chemical behavior results from the interaction of the structural features known as functional groups with either other chemical entities or physical factors such as heat and light. After a description of the chemical components of wood including their relevant functional groups, the most important chemical interactions will be discussed.

Composition of Wood

The chief components of woody plant cell walls are cellulose, hemicelluloses, and lignin. In bark these structural components may be exceeded by suberins and phenolic acids. The final category of wood components is known as extractives. These materials are much less abundant, variable in structure or quantity, usually soluble, and often species or genus specific.

Cellulose

Cellulose is the chief cell wall component, and comprises 40–45% of the wood. It is a long chain polymer of glucose units linked together by glycosidic bonds, a type of acetal ether linkage (O–C–O–C).

The other, and most important, functional group in cellulose is the hydroxyl (–OH). Each glucose unit in the chain has three free hydroxyl groups that are capable of reacting with others in a neighboring chain or with water to form hydrogen bonds (H–O–H—H–O–C). Unlike starch which is also a glucose polymer, but with an α-configuration leading to an amorphous structure, the β-configuration in cellulose leads to stiff and straight chains that can form highly ordered crystalline regions. Cellulose contains disordered or amorphous regions as well.

Hemicelluloses

Associated with the cellulose in the cell wall are carbohydrate polymers known as hemicelluloses. They consist for the most part of sugars other than glucose, both pentoses and hexoses, and are usually branched and of much lower molecular weight than cellulose. In softwoods they comprise 25–30% of the wood in decreasing abundance as mannose, xylose, glucose, galactose, and arabinose. In hardwoods the hemicelluloses account for 20–35% as xylose, mannose, glucose, and galactose. The functional groups as in cellulose are glycosides and hydroxyls, with the addition of acetyl ester groups formed by the reaction of acetic acid with hydroxyls.

Lignin

Lignin is the third major wood cell wall component (20–30%). It serves as a cement between wood fibers, as a stiffening agent within the fibers, and as a barrier to the enzymatic degradation of the cell wall. Lignins are three-dimensional network polymers of phenylpropane units. More than two-thirds of the linkages are ether bonds, the rest are carbon–carbon bonds. Some free phenolic hydroxyls are found on the phenyl groups, but most have been etherified with methanol to methoxyl. Softwood and hardwood lignins differ in methoxyl content and in the degree of crosslinking. Hardwood lignins have more methoxyls, but these groups block potential reactive sites and reduce crosslinking. There is evidence that covalent linkages exist between lignin and the hemicelluloses.

Bark Components

Bark fibers contain cellulose, hemicelluloses, and lignin, but in much lower concentration. The cellulose content may be as low as 20–30%. Two other components unique to bark, suberins and phenolic acids, account for this. Suberins consist of long-chain esters. Their content varies from 2–8% in pine, fir, and oak to 20–40% in birch, and 35–40% in cork oak. Phenolic acids are high molecular weight

phenols, but lower in weight than lignin. They have a high carboxylic acid content, and lower methoxyl content. They may comprise 50% of the weight of conifer bark.

Extractives

Extractives are the extraneous wood components that may be dissolved in water or organic solvents. They are often genus or species specific. Major categories include sugars, fatty acids and their esters, acids, aldehydes, alcohols, terpenes, tannins, quinones, and volatile oils.

Chemical Interactions of Wood and its Components

It is customary in considering the interactions of wood and chemicals to concentrate on the result of the chemical action. The chemical technology of wood is usually divided into such categories as fractionation of wood into its separate components, the conversion of the wood components into various low molecular weight or polymeric products, or the deterioration of wood by chemicals.

However, all these processes possess a common feature. They all begin with the interaction of a chemical reagent with the bonds and functional groups present in the wood. The structures of wood and its components have been defined above. Chemical properties of wood may thus be related to specific reactions of reagents and reactive sites in the wood. Physical factors such as heat, light, and ionizing radiation can also effect chemical changes in wood and its components.

Water

Wood–water relationships are usually considered from a physical or mechanical perspective, involving either drying or dimensional change. However, the underlying phenomenon is chemical in nature, involving the formation of hydrogen bonds between the hydroxyl groups in water and the many hydroxyl groups in the 75% of wood that is carbohydrate in nature.

All the hydroxyl groups are not available for hydrogen bonding and thus adsorption of water. In the crystalline regions of the cellulose, hydroxyls in adjacent linear chains hydrogen bond with each other. This prevents the dissolution of cellulose in water, in contrast to starch whose helical or branched chains cannot bond to each other by hydrogen bonds. In the noncrystalline or amorphous regions of the cellulose, and in the hemicelluloses, the hydroxyl groups are free to bond with water, and

the bound water can bond to more water, leading to adsorptions of up to 30% of the wood weight at the fiber saturation point with commensurate changes in wood volume.

Hydrogen bonds are much weaker than covalent bonds, but in the aggregate they represent large amounts of energy, and require large inputs of heat for their disruption in the drying process in kilns. Even at low relative humidities the driving force of hydrogen bond formation ensures that wood contains appreciable quantities of bound water.

Hydrolysis

Hydrolytic reactions are the most important in their effect on the properties of wood. Both carbohydrates and lignin are susceptible. In carbohydrates the affected groups are the acetal and ester linkages. The acetals are more important because of their greater abundance and their structural role in chain formation. Both acids and alkalis can cause hydrolysis, but the chain scission by acids has the greatest impact on wood properties.

Ester hydrolysis by alkali liberates free hydroxyl groups on the hemicellulose with a reduction in alkalinity in the solution. In acid hydrolysis, however, the liberation of free acetic acid can increase the acidity leading not only to further ester hydrolysis, but also to cleavage of acetal linkages and lignin bonds in the autohydrolysis reaction. At its maximum extent acetic acid liberated by steam can completely hydrolyze the hemicellulose to its constituent monosaccharides and convert the lignin into soluble fragments.

Acid hydrolysis of the acetal linkages in wood polysaccharides proceeds by fission of the glycosyl oxygen bond between the rings. Because of steric factors the rate of hydrolysis of crystalline cellulose is several orders of magnitude less than that of simple glycosides or noncrystalline polysaccharides. However, in the amorphous regions of the cellulose and the hemicelluloses the acetals are subject to ready attack. Under alkaline conditions acetal hydrolysis is much slower and proceeds only at higher temperatures.

Hydrolysis of the lignin linkages under both acidic and alkaline conditions has been studied extensively because of its importance in the pulping of wood. The various ether linkages respond differently to different reagents. Some respond to mild hydrolysis with hot water or dilute acetic acid. Others are cleaved by acid sulfite pulping, while alkaline reagents at elevated temperatures as in Kraft pulping break ether linkages between the phenylpropane units with liberation of phenolic hydroxyl groups. Cleavage of C–C bonds can also occur during acid

hydrolysis, as well as in trace amounts under alkaline conditions.

Oxidation

Both the carbohydrate and lignin components of wood are affected by oxidizing reagents. Mild oxidants such as chlorine, bromine, or iodine convert the aldehyde end groups in the wood polysaccharides to carboxylic acids. Nitrogen dioxide converts primary hydroxyl groups to carboxyl groups. Periodic acid is a specific oxidant for adjacent diols. Stronger oxidants such as nitric acid, potassium dichromate, and potassium permanganate cause extensive degradation of carbohydrates to a series of dicarboxylic acids.

Molecular oxygen in the presence of alkali generates hydroperoxides which can result in stepwise depolymerization of polysaccharides known as peeling. Carbonyl groups are introduced into polysaccharides by the action of chlorine, hypochlorite, and ozone. Hydrogen peroxide and chlorine dioxide react much more slowly and are less degrading, so they are favored in pulp bleaching.

Oxidations of lignin may be placed in three categories: degradation of lignin to aromatic carbonyl compounds and carboxylic acids, degradation of aromatic rings, and oxidation of specific functional groups.

The first category includes oxidations with nitrobenzene, molecular oxygen, or metal oxides under alkaline conditions. Aromatic ring degradation results from exposure to peracetic acid, nitric acid, chlorine, chlorine dioxide, ozone, and the anions of hypochlorous and chlorous acids. Neutral permanganate can oxidize both side chains and rings. Periodic acid and alkali peroxides oxidize specific functional groups. Lignin oxidation is also involved in the photodegradation of wood and the enzymatic degradation of lignin.

Strong oxidants such as permanganate and dichromate in acidic solution degrade lignin completely to carbon dioxide and dibasic acids. A group of oxidants between the strong ones and the side chain oxidants, attack primarily the aromatic nuclei of the lignin. Because they show a relative selectivity in attacking lignin more rapidly than carbohydrate, chlorine, nitric acid, chlorine dioxide, sodium hypochlorite, peracetic acid, hydrogen peroxide, and ozone have found utility in the bleaching of the residual lignin in pulp after removal of most of the lignin by pulping.

Decrystallization

The crystallinity of cellulose is an inherent property that governs its mechanical properties, affinity for water, and accessibility to chemical reagents. Since the crystallinity is the result of interchain hydrogen bonding, changes in crystallinity reflect decreases or increases in this bonding.

Although water alone cannot break the interchain hydrogen bonds, decrystallization can be brought about by many reagents. The extent of decrystallization may vary from partial swelling to increase chemical accessibility to complete dissolution that permits reprecipitation and the formation of regenerated cellulose fibers such as rayon.

These reagents include concentrated sodium hydroxide; amines; metalloorganic complexes of copper, cadmium, and iron; quaternary ammonium bases; concentrated mineral acids (sulfuric, hydrochloric, phosphoric); concentrated salt solutions (beryllium, calcium, lithium, zinc); and mixtures of organic solvents.

An increase in crystallinity is unusual, but it does occur after hydrolysis of amorphous cellulose. The broken chains have greater freedom to form more highly organized structures.

Discoloration

Staining or discoloration of wood may result from chemical processes that convert originally colorless or light-colored, naturally occurring extractives into intensely colored products.

Most of the so-called chemical stains result from oxidation of certain wood extractives by air during air seasoning or kiln drying. Colors observed include shades of brown, blue, green, yellow, and red. Affected species include both hardwoods (oak, birch, maple, alder, basswood, gum, etc.) and softwoods (pines, hemlock).

Wet wood can also discolor by contact with iron or copper when tannins are present to form black iron tannate or reddish copper tannate. These metals may also initiate oxidation of the wood by free radical mechanisms.

Other Functional Group Reactions

The functional groups in wood and its components can also enter into the normal reactions of the various groups. Thus hydroxyl groups may undergo esterification or etherification. Cellulose esters of both inorganic and organic acids are important industrial products, most notably cellulose nitrate and cellulose acetate. Cellulose ethers such as methylcellulose and carboxymethylcellulose are also important. These reactions have also been carried out on whole wood. Organic chemicals that have been used to react with the hydroxyl groups include acid anhydrides and chlorides, aldehydes, alkyl

chlorides, carboxylic acids, epoxides, isocyanates, lactones, and nitriles.

The carboxylic acid and phenolic hydroxyl groups in wood contribute to its natural acidity. These acidic groups can act as ion exchange agents with sodium in alkaline solutions, or with copper and zinc in wood-preserving solutions.

Reducing end groups such as aldehydes in wood sugars are the agents which convert hexavalent chromium in some wood preserving formulations to insoluble forms.

Surface Chemistry of Wood

The utilization of wood and wood fibers involves in more cases than not the interaction of the woody material with natural and synthetic polymers in the form of adhesives and coatings. The chemistry of the wood surface may influence the conversion of liquid formulations to solid form, and certainly plays a critical role in the wetting and bonding of these substances to the wood surface. Aside from the bonding forces themselves, such factors as pH, moisture content, and extractives have a direct influence on bonding.

The bonding forces may be of three types. London, van der Waals, or dispersion forces act between all atoms and are mainly responsible for the cohesion of all materials. Dipole–dipole interactions between positive and negative charge centers are especially important in wood with its many hydroxyl groups. In the hydrogen bond the positive proton is shared between two electronegative atoms, most frequently nitrogen or oxygen. Finally, true chemical bonds, either covalent or ionic, may form between the functional groups in the wood and those in the coating or adhesive.

Most important resins used with wood are of the thermosetting type whose cohesive strength exceeds that of the wood. They include urea–formaldehyde, melamine–formaldehyde, phenol–formaldehyde, di-isocyanates, polyisocyanates, and polyamides. Their polar groups can form strong hydrogen bonds with the hydroxyl groups in wood, and their functional groups can interact with the wood.

The polymeric adhesives and coatings are generally applied in liquid form, and then cured to solids. The acidity of some species of wood can interfere with these reactions, especially those that are base catalyzed. Both soluble and insoluble acids have been implicated. Wood extractives that compete with the resins for formaldehyde can also disrupt the curing process.

Modification of the wood surface to introduce more functional groups capable of covalent bond formation has been studied. Activation of the surface by heat, acids, or oxidants may be followed by three approaches. Direct covalent bonds may be formed between two wood surfaces. Bifunctional monomers may be used to join the surfaces. And finally, polymeric chains may be used to bridge the surfaces.

Chemical Effects of Physical Factors

The chemical properties of wood and the wood itself may be modified by physical factors. Heat is most important, but light and ionizing radiation also cause changes in the wood chemistry.

Heat

Chemical reactions involve the breaking of bonds in the reactants and the formation of new bonds in the reaction products. These processes are accelerated by thermal energy or heat since the bonds represent states of minimum energy. However, even in the absence of external reagents the chemical bonds holding molecules together are subject to scission and rearrangement when sufficient thermal energy is applied.

In the case of wood a description of the effect of heat is complicated by the variations in composition between species. Examination of the behavior of the individual components can provide insights that may be extended to whole wood.

As wood is heated above room temperature the water adsorbed by the hygroscopic wood components is first driven off. At higher temperatures the wood components start to decompose with the evolution of gases. Hemicelluloses show initial decomposition at about 120°C, lignin above 130°C, and cellulose above 160°C. The gases evolved during this slow, low-temperature pyrolysis are not flammable. Water vapor and carbon dioxide predominate, with lesser amounts of carbon monoxide and traces of organic acids being present. It is evident that dehydration and decarboxylation are taking place. Wood that has been heated above the boiling point of water for extended periods becomes less hygroscopic and more dimensionally stable with some sacrifice of strength.

Above 200°C the rate of decomposition increases until rapid exothermal weight losses occur at 260°C, 280°C, and 330°C, probably representing the different behavior of the separate wood components. With the onset of rapid pyrolysis, flammable gases are evolved such as carbon monoxide, methane, formaldehyde, formic and acetic acids, and methanol. Also evolved are highly flammable tars containing furfural and other furan derivatives from the decomposition of pentosans, levoglucosan from the

decomposition of the cellulose, and aromatic fragments such as phenols, xylenols, guaiacols, cresols, and catechols from the decomposition of the lignin.

In the presence of air these flammable gases and tars evolved during rapid pyrolysis can further react with oxygen in the process we call burning, adding their heat of combustion to the degradation process, and intensifying it. The residue becomes charcoal, with carbonization becoming complete at 400–500°C and the crystalline structure of graphite developing.

In the presence of acidic or alkaline compounds the decomposition takes a different course. Instead of the liberation of flammable gases and tars the modified pyrolysis leads to increased amounts of charcoal by dehydration of the cellulose and hemicelluloses. The increased char formation occurs at the expense of flammable volatile tars. The cellulose is preferentially converted to carbon and water. When this dehydration occurs at temperatures below the normal decomposition temperature of wood, the wood has been effectively flameproofed.

Light

Exposure to light causes photodegradation and photooxidative degradation. Ultraviolet light interacts with lignin resulting in discoloration and deterioration. In a surface phenomenon, since light does not penetrate beyond 200 μm, the free radicals generated interact with oxygen to form hydroperoxides which in turn decompose. The results are large color changes and chemical degradation.

Wood is an excellent light absorber. Cellulose absorbs strongly below 200 nm. Hemicelluloses are structurally similar, so their ultraviolet absorption characteristics resemble those of cellulose. Lignin and polyphenols absorb light strongly below 200 nm and have a strong peak at 280 nm, with absorption continuing through the visible region. Extractives absorb between 300 and 400 nm.

The strong absorption of ultraviolet light by lignin results in preferential lignin degradation. The process is initiated by the formation of free radicals, and begins with the oxidation of phenolic hydroxyls. Methoxyl and lignin content decrease, while acidity and carboxyl content increase. The products of decomposition, in addition to gases and water, are mainly organic acids, vanillin, syringaldehyde, and higher molecular weight, but water soluble, compounds.

The color of wood exposed to light changes rapidly. Woods rich in extractives may become bleached before photooxidation of lignin results in a loss in brightness. The general change in color in all woods is toward a yellow to brown as degradation

proceeds. The yellowing of newsprint after brief exposure to light is typical behavior. The final gray color seen in wood exposed to light for long periods of time represents residual cellulose after degradation and removal of most of the lignin.

Ionizing Radiation

High energy radiation can depolymerize the wood components by creating free radicals along the C–C backbone. If two free radicals are formed on separate chains in close proximity, crosslinking can take place. If the free radicals are created near a reactive or functional group other types of reactions can occur. When the free radical is on a tertiary carbon, disproportionation with chain scission can take place.

Surprisingly, lignin is more resistant to gamma-radiation than cellulose, even though it is more susceptible to the lower energy ultraviolet radiation. Irradiated cellulose is degraded by the cleavage of glycosidic bonds. But the radical sites created on the cellulose at lower levels of irradiation have been used for initiation of grafting on the cellulose and copolymerization in the presence of vinyl monomers.

High-energy radiation in the form of gamma-rays and X-rays can penetrate wood readily, whereas photoirradiation is only a surface phenomenon from ultraviolet penetration of up to 75 μm and visible light penetration of up to 200 μm. Thus extended high-energy radiation can be very destructive. White oak wood irradiated to 1900 Mrad with gamma-rays had an increase in extractives from 9% to 69% showing extensive solubilization. Holocellulose was reduced from 58% to 4%, while lignin showed only a slight loss from 33% to 27%.

See also: **Non-wood Products**: Chemicals from Wood. **Solid Wood Processing**: Chemical Modification. **Tree Breeding, Practices**: Biological Improvement of Wood Properties. **Wood Formation and Properties**: Formation and Structure of Wood; Wood Quality. **Wood Use and Trade**: History and Overview of Wood Use.

Further Reading

Browning BL (ed.) (1963) *The Chemistry of Wood*. New York: John Wiley.

Hon DNS and Shiraishi N (eds) (2001) *Wood and Cellulose Chemistry*. New York: Marcel Dekker.

Lewin M and Goldstein IS (eds) (1991) *Wood Structure and Composition*. New York: Marcel Dekker.

Rowell R (ed.) (1984) *The Chemistry of Solid Wood*. Washington, DC: American Chemical Society.

Sjostrom E (1981) *Wood Chemistry*. New York: Academic Press.

Wenzl HFJ (1970) *The Chemical Technology of Wood*. New York: Academic Press.