

## CHAPTER II

### THEORY

#### 2.1 Wood Composite

Wood composites refer to any composites that is a combination of two materials (a filler as woodflour or natural fiber and a matrix as thermosets or thermoplastics), differing in form or composition on a macroscale. The combination results in a material that maximizes specific performance.

Over the 20-year period ending in 1994, the world population increased by 40 percent. In that same period, global consumption of wood increased 37%. This per capita demand varied slightly between 0.66 and 0.67 m<sup>3</sup>. If the demand for wood continues we continue at this rate, it will be necessary to increase the production of wood products by 0.3-0.7 billion m<sup>3</sup> per decade for the next 4-6 decades. Since the current total annual wood harvest globally is approximately 3.5 billion m<sup>3</sup>, the anticipated increase in the demand is significant. In addition, during the 1980's, there was a decrease of 2% in the world's forest due to deforestation excluding the forest that was logged and left to regenerate. Consequently, composites made of wood and plastics are recently finding their way into the market as wood substituted materials. In 1998, the North American market for wood composite plastics was 565 million pounds and valued at US\$220 million. This market is expected to grow at 13% per year from 1998 to 2008 [D.A. Johnson *et al.*, 1999].

Wood is one of the oldest construction materials in human history and continues to be an extremely valuable material to this day. Wood is lightweight, strong, easily worked and fastened, a good insulator, warm to the touch, and pleasing in its appearance, among many other attributes [J.A. Youngquist *et al.*, 1999]. On the other hand, wood shows rather high water uptake, high flammability, and poor termite resistibility. Due to

the strong demand on wood and the aims to overcome those drawbacks of natural wood, a wood substituted material using waste wood and polymeric binders has been developed and gained worldwide attention. These kinds of wood composites exhibit their tailor made characteristics from the tremendous variety of the polymer matrices to be utilized as wood binders. In this investigation, fire resistant resins based on benzoxazine alloys are developed as a binder for *hevea brasiliensis* woodflour and the expected fire resistant improvement of the resulting composites is evaluated.

## 2.2 Fire Resistant Wood Composites

Fire safety is an important concern in all types of construction. Fire prevention basically means the elimination or suppression of an ignition of combustible materials by controlling either the source of heat or combustible materials.

Due to its hydrocarbon nature of its molecular constituents, wood will burn when exposed to heat and air. Thermal degradation of wood occurs in stages. The sequence of events for wood combustion is as follows [Robert H. White and Mark A. Dietenberger, 1999]:

1. Wood, responding to heating, decompose or pyrolyzes into volatiles. They become much more pronounced above 300°C.
2. Volatiles, some of which are flammable, can be ignited if the volatile-air mixture is of the right composition in a temperature range of about 400°C to 500°C. This gas-phase combustion appears as flame.
3. With air ventilation, the char oxidation becomes significant around 200°C. This char oxidation is seen as glowing or smoldering combustion until only ash residue remains. This solid phase combustion will not proceed if flaming combustion prevents a supply of fresh air to the char surfaces.

Several characteristics are used to quantify the burning behaviors of wood composites including limiting oxygen index (LOI), burning rate, heat of combustion (HOC), smoke generation, and heat release rate (HRR).

## Limited Oxygen Index

The standard practice of this analysis is disclosed in ASTM D 2863-95. In the test, a 70 to 150 mm long, 6.5 mm wide, and 3 mm thick vertical sheet of a material is placed inside a glass cylinder, with gas flowing in an upward direction. The test is performed at various oxygen concentration under ambient temperature, with sample ignited at the top, to determine the minimum oxygen concentration at or below which there is no downward flame spread. The minimum oxygen concentration is defined as the limiting oxygen index (LOI) of the material and can be quantified using the following equation.

$$\text{LOI (\%)} = (100 \times \text{O}_2) / (\text{O}_2 + \text{N}_2) \quad 2.1$$

where LOI = Limiting oxygen index

$\text{O}_2$  = Volumetric flow of oxygen,  $\text{mm}^3/\text{s}$

$\text{N}_2$  = Volumetric flow of nitrogen,  $\text{mm}^3/\text{s}$

Examples of LOI values measured at ambient temperature for various materials are listed in Table 2.1.

**Table 2.1** Ambient temperature limiting oxygen index (LOI) values for some important materials [C.A. Harper, 2004, G.L. Nelson, 2001, A.H. Landrock, 1983]

Materials	LOI	Materials	LOI
Cellulose acetate	17	Urea-formaldehyde	30
Polypropylene	17	Polysulfone	31
Polyethylene	18	Polyvinyl chloride	37-42
Polystyrene	18	Polyaramide (Kevlar®)	38
Epoxy	20-35	Phenolic	41
Plywood	23	Polyetherimide	47
Polybenzoxazine (BA-a)	30	Polytetrafluoroethylene	95

## Char Yield

Char is the carbonaceous solid that remains after flaming combustion of the substance. The char yield is the mass fraction of char based on the original weight of material. Charring competes with the termination reactions that generate volatile species and so reduces the amount of fuel in a fire. In addition, char acts as a heat and mass transfer barrier that lowers the flaming heat release rate. The char yield in a fire is roughly equal to the anaerobic pyrolysis residue at high (flame) temperatures. Thus, char formation takes place in the solid state where oxidation reactions are slow compared to polymer dissociation and gas/char formation. The equivalence between the char yield and pyrolysis residue of a material permits a molecular interpretation of this important material fire parameter using the large volume of published thermogravimetric data and its correlation with chemical structure [D.W.V. Krevelen, 1975].

Pyrolysis/char residue has a character of a thermodynamic quantity because it depends only on temperature and the composition of the material through the enthalpy barriers to gas and char formation. More precisely, char yield is a statistical thermodynamic concept wherein the total free energy of the char system at a particular temperature is the sum of the individual group contributions. D.W.V. Krevelen, 1975 has devised a method for calculating the pyrolysis residue (char yield) of a polymer from its chemical composition and the observation that the char-forming tendency of different groups is additive and roughly proportional to the aromatic (i.e., nonhydrogen) character of the group.

### **Stages in Burning of Plastics [A.H. Landrock, 1983]**

The burning of a solid polymer or a polymer composite involves four stages.

1. Heating of the polymer
2. Thermal decomposition
3. Ignition
4. Combustion

## 1. Heating of the polymer

Heat source, such as flame, raises temperature of a polymer at various rates depending on the relative sizes and temperatures of the flame and of the polymer. During this initial stage, thermoplastic materials soften or melt and begin to flow. The temperature at which melting occurs can have a pronounced effect on the subsequent stages in the process. The amorphous or crystalline linear polymers begin to lose their rigidity at the glass transition temperature or the melting temperature, respectively, and a continuous decrease in the viscosity of the melt takes place up to the decomposition point. Whereas thermal behaviors of thermosets or crosslinked polymers primarily vary with their degree of crosslinking. The thermal properties of polymers are mainly characterized by the glass transition ( $T_g$ ) and melting temperatures ( $T_m$ ). The values of these parameters are listed in Table 2.2.

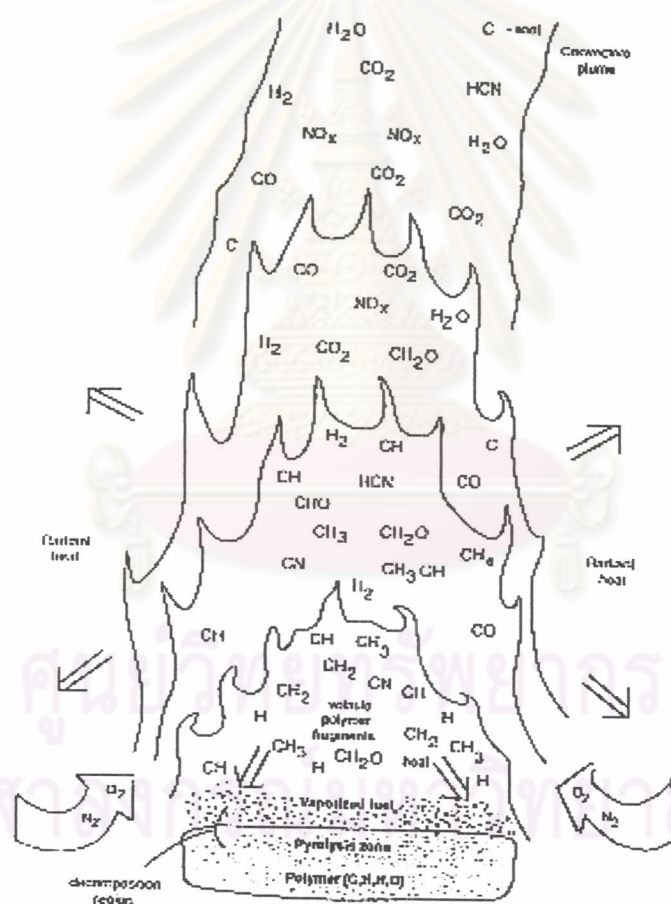
**Table 2.2** Glass transition temperature and melting temperature of some polymers  
[C.A. Harper, 2004]

	Temperature ( $^{\circ}\text{C}$ )	
	$T_g$	$T_m$
Low density polyethylene	-125	105-110
High density polyethylene	-	130-135
Polypropylene (atactic)	-20	160-165
Polyvinyl chloride	81	189
Polypropylene (isotactic)	100	-
Polystyrene	100	-
Phenolic Novolac	121	-
Polybenzoxazine (BA-a)	165	-

## 2. Thermal Decomposition

In later stage, decomposition of the plastic with the elimination of volatile gases or chemically degraded polymer fragments occurs as shown in Figure 2.1. The

temperature and the rate at which this phenomenon occurs depend upon thermal stability of the polymer and the chemical decomposition reactions involving under the existing conditions. Thermosetting plastics represent a unique class as their decomposition is more complicated, with chemical fragmentation occurring to produce a variety of decomposition products. Other polymers, such as polyvinyl chloride, degrade by the elimination of small volatile fragments, such as HCl. Decomposition of this type introduces a considerable amount of unsaturation into the polymer chain, which complicates the subsequent oxidative processes. Plastics degrade thermally in a different manner in inert atmosphere than they do under oxidative conditions which further results in more complex reactions.



**Figure 2.1:** Schematic representation of thermal degradation of polymers  
[G.L. Nelson, 1995].

The decomposition and charring characteristics of materials depend on their thermal stability (chain rigidity and strong interchain forces), characterized by the decomposition temperatures ( $T_d$ ) and the char yield. The values of these parameters of some polymer are listed in Table 2.3.

**Table 2.3** Decomposition temperature and char yield of some polymeric materials

[C.A. Harper, 2004]

Materials	$T_d$ ( $^{\circ}\text{C}$ )	Char yield (%)
Polystyrene	364	0
Polypropylene	320-400	-
Polyurethane	422	3
Polyethylene	340-440	0
Polyvinylchloride	270	11
Epoxy	427	-
Phenolic Novolac	343	55-70
Polybenzoxazine (BA-a)	334	25-30

There are fire major factors controlling thermal stability of polymeric materials. In general, higher molecular weight with lower degree of chain branching result in an improvement in the stability in thermoplastics polymers. The greater the degree of crosslinking, the more stable the thermosetting polymers from thermal decomposition. In addition, the presence of the unsaturated bonds cause the thermal weakening whereas the incorporating of the aromatics into the polymer structure helps enhance thermal stability of the materials.

### 3. Ignition

When temperature of a polymer increases and the resulting flammable gases reach an appropriate ratio to oxygen of air, ignition occurs. Whether burning continues is dependent upon the transfer of sufficient heat from the flame to the polymer to maintain a supply of flammable gaseous decomposition products, and upon a supply of oxygen from

the surrounding atmosphere sufficient to support combustion. A continuous propagating flame will not be obtained if decomposition of the polymer requires more heat than that supplied by the flame, or if nonflammable solid residues coat the surface and insulate the remainder of the flammable composition from the heat source.

#### 4. Combustion

The characteristics of the polymer in this stage may be correlated with energy relationships in the molecule. The net thermal effect of combustion can be either negative or positive. If negative, an external supply of heat is needed to support combustion. If positive, the excess of heat is made available to increase the temperature of the adjacent material. The most important energy factors are cohesive energy, hydrogen bonding, heat of combustion, and dissociation energy. Einhorn divides the combustion stage into three substages:

**Nonflaming Degradation:** Many materials will degrade or smolder by a nonflaming degradation. In fact, some materials do not combust at all in normal oxygen environments.

**Flame Propagation:** Propagation results when the net heat of combustion is sufficient to bring the adjacent mass to the combustion stage. The ease with which the material is brought to this stage depends on its chemical structure, geometry and attitude. An oxidizing agent is generally required to sustain combustion. Some materials release oxygen while degrading, and are then capable of supporting combustion at a limiting oxygen index (LOI) of less than 21%. Other materials require oxygen from the environment to support combustion.

**Physical Response (Shrinkage, Melting and Char Formation):** Synthetic fabrics, such as polyamides (nylons) and polyesters shrink considerably at relatively low temperature. This shrinkage can be serious in clothing fires. The burning droplets from melting synthetics can make particularly deep and serious burns. Some polymers, including rigid urethane foams, form char structures during burning. These polymers possess a high degree of aromaticity and crosslink densities of less than 340. When the



crossing density exceeds 400, intumescence and slight melting occurs. At crossing densities over 500, there is evidence of char formation and combustion is complete.

### **2.3 Thermosetting Resins [A.H. Landrock, 1983]**

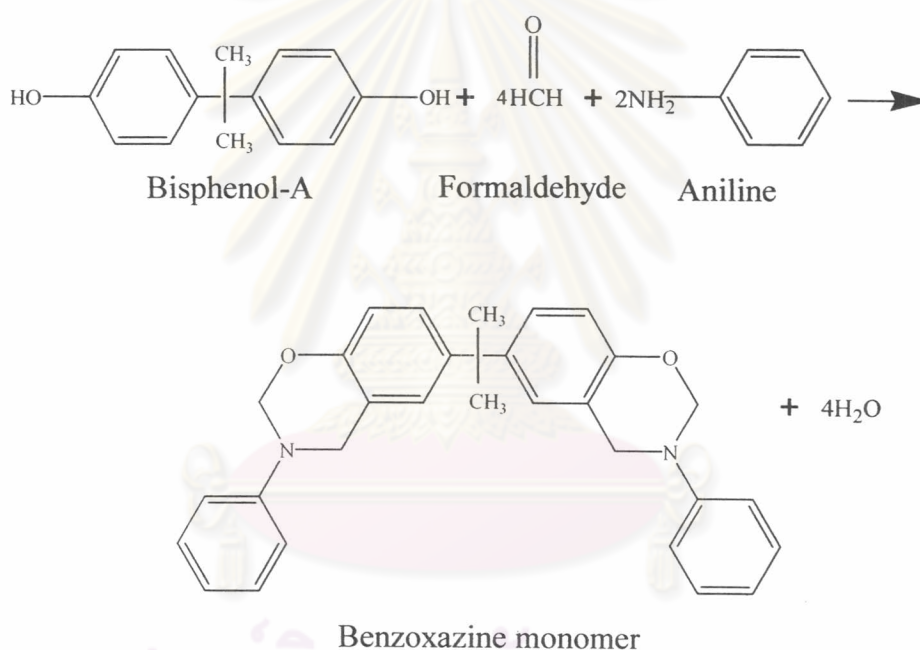
Thermosetting polymers differ from thermoplastics in that they become chemically crosslinked during final molding and curing. For most practical purposes they can no longer be melted, reshaped or dissolved. Thermosetting resins are produced in large volume and extensively used in the construction, housing, and large appliance industries where they may contribute significantly to the fire load in any particular area or product. For this reason their fire safety characteristics are important. Because of their crosslinked nature thermosets generally do not soften or drip when exposed to a flame, as do many thermoplastic materials. Their flammability is a function of the thermal stability of the primary chemical bonds and the ease with which volatile gaseous products can be produced by pyrolytic processes to provide fuel for a self-sustaining fire. Many thermosets (e.g. the phenolic resins) produce very little flammable fuel when heated by an ignition source. They produce an insulating char that can only be oxidized at extremely high temperature and high oxygen concentration. Burning of such materials can be a slow process under many conditions since the polymer substrate is protected by the surface char. Such resins are inherently fire-retardant and will pass many common laboratory tests without the need for a fire-retardant modification or additive. Their fire retardance is; however, a function of the mechanical ability of the insulating char and is limited by the resistance of elemental carbon to oxidation. Other thermosets (e.g. styrenated polyester resins) do not form chars and burn readily.

### **2.4 Benzoxazine Resin**

Polybenzoxazine is a newly developed thermosetting resin with interesting properties. As a novel class of phenolic resins, it has been developed and studied to overcome the shortcomings of the traditional novolacs and resoles. Polybenzoxazine has

excellent properties commonly found in traditional phenolic resins such as high thermal stability, flame retardance, dimensional stability, near-zero shrinkage, low viscosity, low water absorption. In addition, they can be synthesized from inexpensive raw materials and can be cured without the use of strong acid or base catalyst. The crosslinking reaction of the resin is through thermally activated ring-opening reaction; therefore, do not release by-products during the polymerization [T. Takeichi *et al.*, 2002]. Consequently, the polymer is a highly attractive candidate for various applications.

Benzoxazine resin based on bisphenol-A and aniline is synthesized according to the following reaction scheme (Figure 2.2) [X. Ning and H. Ishida, 1994].



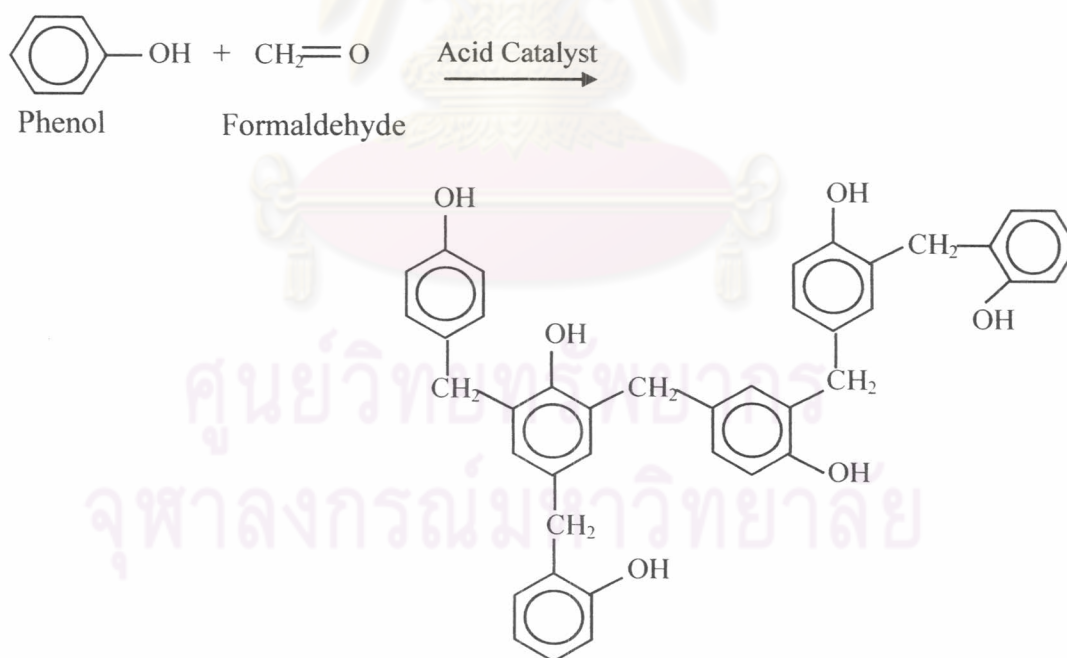
**Figure 2.2:** Synthesis of benzoxazine resin.

## 2.5 Phenolic Resin

Phenolic resins are one of the most popular condensation polymers. They are widely used in industry because of their outstanding flame and chemical resistance, electrical insulation, and dimensional stability [A. Gardziella *et al.*, 1999]. The resins are

usually made from the condensation polymerization of phenol and formaldehyde, thus give them another name, phenol formaldehyde resins.

There are two major categories of phenolic resins, which are classified by their structure and curing properties: resol and novolac. Although these two types of phenolic resins are similarly produced by phenol and formaldehyde, the catalyst and the composition of original phenol to formaldehyde mass ratio used in the preparation process are different. The resultant resins, consequently, have different structure that affect their curing properties. In this study, phenolic novolac resin is used to form polymer alloys with the benzoxazine resin. Novolac is produced from the condensation reaction of phenol and formaldehyde using acid as a catalyst. This resin contains no reactive methylol groups in its molecule. Therefore, it is, upon heating, unable to be cured by itself to form a crosslinked resin. In order to cure novolac, a reactive methylene containing substance, a curing agent, such as hexamethylenetetramine, must be added. The molecular structure of the phenolic novolac is shown in Figure 2.3.



**Figure 2.3:** Synthesis and molecular structure of phenolic novolac resin.

The advantages of using phenolic novolac resin as wood binder are their known high compatibility with wood, high char yield, no toxic by products from burning, and its low cost. The addition of phenolic resin can sometimes significantly enhance fire resistant properties of the base polymers it is with incorporated.

However, there exist some drawbacks of typical phenolic novolac such as the need for coming agent, the releasing of the condensation reaction by-products, and relatively hydrophilic in nature.

## 2.6 Wood

The fibrous nature of wood strongly influences how it is used. Wood is primarily composed of hollow, elongate, spindle-shaped cells that are arranged parallel to each other along the trunk of a tree. When lumber and other products are cut from the tree, the characteristics of these fibrous cells and their arrangement affect such properties as strength and shrinkage as well as the grain pattern of the wood. The basic wood elements that can be used in the production of wood composites are shown in Figure 2.4.

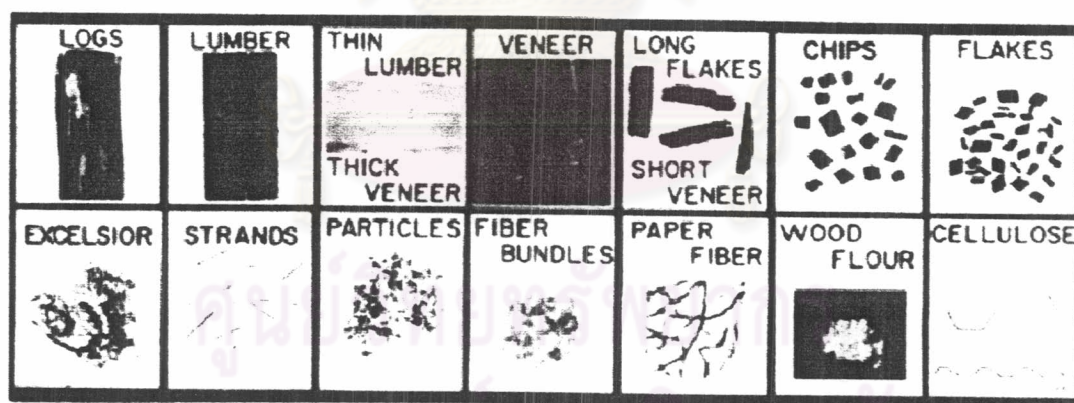
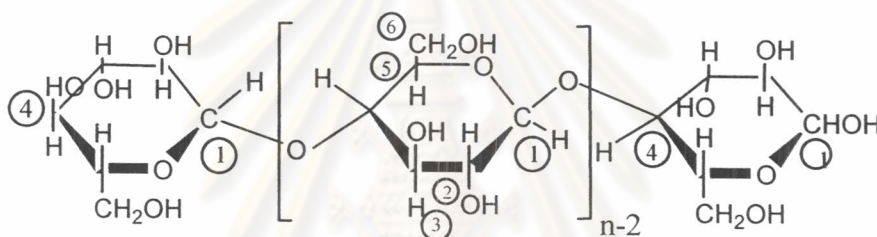


Figure 2.4: Basic wood elements from largest to smallest [J.A. Youngquist *et al.*, 1999].

Dry wood is primarily composed of cellulose (60-80%), lignin (2-15%), hemicelluloses (5-20%), and minor amounts of extraneous materials (5-10%) [R.B. Miller, 1999].

## Cellulose

Cellulose, the major component, constitutes approximately 50% of wood substance by weight and up to 80% by weight in natural fiber. It is a high-molecular-weight linear polymer consisting of chains of 1-4  $\beta$ -linked glucose monomers up to about 8000 repeating units. During growth of the tree, the cellulose molecules are arranged into ordered strands called fibrils, which in turn are organized into the larger structural elements that make up the cell wall of wood fibers. Most of the cellulose cell wall is crystalline. Delignified wood fibers, which consist mostly of cellulose, have great commercial value when formed into paper. Delignified fibers may also be chemically altered to form textiles, films, lacquers, and explosives. The formula of cellulose is given in Figure 2.5.

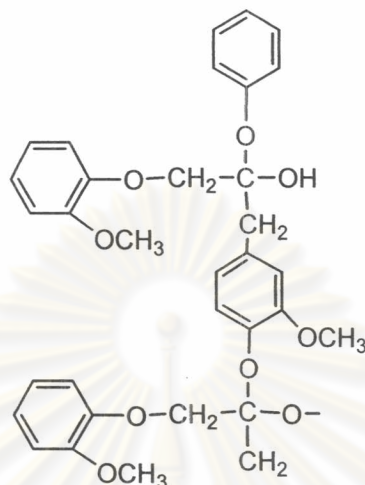


**Figure 2.5:** Molecular structure of cellulose [A.K. Bledzki and J. Gassan, 1999].

## Lignin

Lignin constitutes 23% to 33% by weight of the wood substance in softwoods and 16% to 25% by weight in hardwoods. Although lignin occurs in wood throughout the cell wall, it is concentrated toward the outside of the cells and between cells. Lignin is often called the cementing agent that binds individual cells together. Lignin is a three-dimensional phenylpropanol polymer and its structure and distribution in wood are still not fully understood. On a commercial scale, it is necessary to remove lignin from wood to make high-grade paper or other natural fiber products. Theoretically, lignin might be converted to variety of chemical products, but in commercial practice, a large percentage of the lignin removed from wood during pulping operation is a troublesome by-product, which is often burnt for heat. One sizable commercial use for lignin is in the formulation

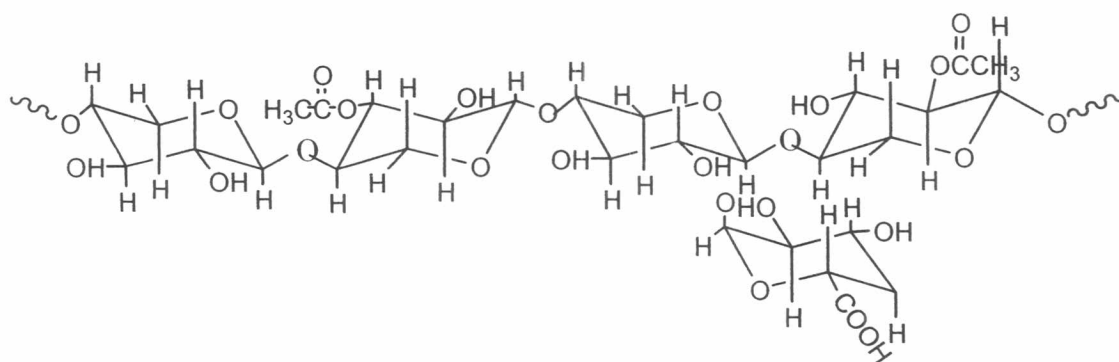
of oil-well drilling muds. Lignin is also used in rubber compounding and concrete mixes. Lesser amounts are processed to yield vanillin for flavoring purpose and to produce solvents. Current research is examining the potential use of lignin in the manufacture of wood adhesives. The formula of lignin is given in Figure 2.6.



**Figure 2.6:** Molecular structure of lignin [A.K. Bledzki and J. Gassan, 1999].

### Hemicellulose

Hemicellulose is associated with cellulose and is branched, low-molecular-weight polymers composed of several different kinds of pentose and hexose sugar monomers. Its degree of polymerization is about 10-100 times less than that of cellulose. The relative amounts of these sugars vary markedly with species. Hemicelluloses play an important role in fiber-to-fiber bonding in the papermaking process. The component sugars of hemicellulose are of potential interest for conversion into chemical products. The formula of hemicellulose is given in Figure 2.7.



**Figure 2.7:** Molecular structure of hemicellulose [A.K. Bledzki and J. Gassan, 1999].

### Extraneous materials

Unlike the major constituents of wood, extraneous materials are not structural components. Both organic and inorganic extraneous materials are found in wood. The organic component takes the form of extractives which contribute to such wood properties as color, odor, taste, decay resistance, density, hygroscopicity, and flammability. Extractives include tannins and other polyphenolics, coloring matter, essential oils, fats, resins, waxes, gum starch, and simple metabolic intermediates. This component is termed extractives because it can be removed from wood by extraction with solvents such as water, alcohol, acetone, benzene, or ether. Extractives may constitute roughly 5% to 30% of the wood substance, depending on such factors as species, growth conditions, and time of year when the tree is cut.

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