

CHAPTER II

THEORITICAL CONSIDERATION AND LITERATURE REVIEWS

2.1 Introduction to Adhesives

An adhesive may be defined as a material which when applied to surfaces of materials can join them together and resist separation. It may develop surface adhesion or internal strength (adhesion or cohesion) without the structure of the bodies undergoing significant changes. The term "adhesive" is a generic term and covers other common terms, such as "glue," "paste," "gum," "adhesive cement," and "bonding agent." The materials being joined are commonly referred to as the "substrates" or "adherends". The latter term is sometimes employed when the materials are apart of a joint [10,11].

The term adhesion is used when referring to the state in which two surfaces are held together by interfacial forces which may consist of molecular forces, chemical bonding forces, interlocking action, or combinations of these. And cohesion refers to the state in which the particles of the adhesive (or the adherend) are held together by forces of adhesion [12,13].

The level of adhesion forces which are operating across an interface cannot usually be measured by mechanical tests. For example, the measured energy for interfacial fracture is generally orders of magnitude higher than that arising solely

from the intrinsic adhesion forces, such as molecular van der Waals' forces or covalent bonds, which may be operating across the interface.

2.1.1 Basic Principles [14]

Adhesion is defined as the state of holding together two surfaces of bodies (adherends) by interfacial forces which can be valence forces or mechanical interlocking or a combination of both (section 2.1.4)

Valence forces which are responsible for the surface attraction, can be either primary valence bonds or secondary valence bonds.

Primary valence bonds are the well known covalent, coordinate, electrovalent, or metallic bonds which are formed when atoms or molecules either share or transfer electrons. their bonding forces range from 10-100 kcal/mole.

Far more important from the standpoint of adhesives, however are the weaker secondary bonds known as Van der Waal force (2-4 kcal/mole). These forces are responsible for the cohesion of non-polar liquid molecules, for example. Also, these weak forces can provide good adhesion between two surfaces ; however in order for these forces to act, molecules must be between 3 to 10 \AA . Beyond 10 \AA , these forces are no longer effective in that they decrease at a rate equal to the sixth power of the intermolecular distance. Even the smoothest of two solid surfaces cannot have enough surface area at intimate contact to achieve any adhesion between the two solids.

This is because the apparent are not at all smooth surfaces at the microscopic level as shown below.

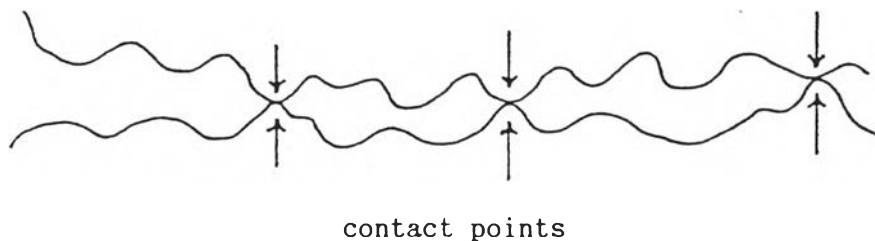


Figure 2.1 Contact points at the microscopic level of smooth surface

This is where the role of the adhesive comes in. Most all adhesives, whether they are chemical reaction types, evaporation types, hot melts, etc, are applied to the adherend in a liquid state. The application as a liquid is necessary in order to sufficiently "wet" the surface of the adherend. This allows the adhesive molecules to get in close proximity to the surface molecules of the adherend in order to establish valence forces. Therefore, it is imperative that the adhesive being applied have sufficiently low viscosity to allow the adherend surface to be wetted properly. If the viscosity of the adhesive is too high, then it will not penetrate properly into the surface pores and crevices. This is important in that if gas bubbles or void occur between the glue line and the adherend, stress will be concentrated more in a smaller area, thus weakening the strength of the bond. It is common practice in

weakening the strength of the bond. It is common practice in adhesive technology to clean and roughen the surface of an adherend before the application of adhesive. This is done not only to remove oxides from a metallic surface, but because a rough surface provides greater joint strength as well as helping to prevent crack propagation along the glue line by isolating air pockets that may have formed from incomplete wetting. The roughness provides "teeth" to the bonded joint. While the adhesive is still a liquid, it displays no cohesive strength to the bond. With cooling, vaporization of a carrier, or through a polymerization reaction, the adhesive will later become a solid which will then provide the cohesive strength to the bond.

2.1.1.1 Thermodynamic of Bonding

In order for a given adhesive to effectively wet an adherend surface, that adhesive must be compatible with the adherend if a lasting bond is to result. Thermodynamically, for a bond between an adherend and an adhesive to be strong, there must be a resulting decrease in free energy (ΔG) from the combination of adhesive and substrate. In other words, the ΔG must be negative in the following equation (2.1).

$$\Delta G = \Delta H - T\Delta S \quad (2.1)$$

where ΔG = Change in free energy ΔS = Change in entropy
 ΔH = Change in heat of mixing T = Temperature

In general, when adhesive and adherend meet, entropy is increased (more disorder), so entropy only contributes to the loss of free energy. Therefore, only the heat from mixing (ΔH), can prevent a negative ΔG from resulting. Thus, provided that the heat of mixing is not too great, the adhesive and adherend will combine. This is even more likely at elevated temperatures. Another way to look at it, is to say for the adhesive to work, the adhesive attraction between the liquid adhesive and the adherend must be greater than the cohesive forces within the liquid adhesive being applied. The following are examples of a "good" and "bad" adhesive bond (figure 2.2).

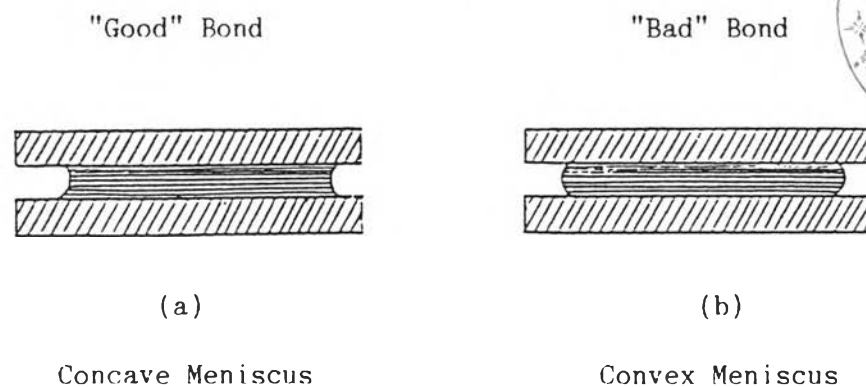


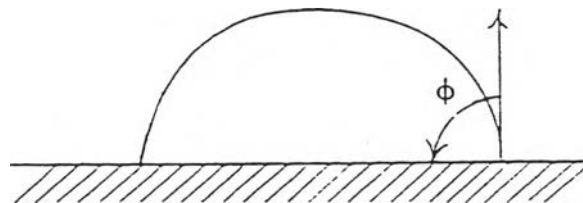
Figure 2.2 Good and bad attraction between the liquid adhesive and the adherend

In figure 2.2(a), the adhesive forces exceed the cohesion forces of the wet adhesive. Therefore, the adhesive spreads over the adherend and "wets" the adherend surface. In figure 2.2(b), the cohesive forces of the wet adhesive are greater than adhesive forces between the adhesive

and adherend. Therefore, in figure 2.2(b) the adhesive is not compatible to the adherend material.

2.1.1.2 Surface Tension

One method to help determine the compatibility between an adhesive and a given substrate was explored by W.A. Zisman of the Naval Research Laboratory in Washington, D.C. Zisman and his colleagues measured the critical surface tensions (γ_c) of different selected polymer surfaces. This critical surface tension measures the "wettability" of a given solid surface. γ_c gives the maximum surface tension that an adhesive can have. If the adhesive surface tension exceeds γ_c , it will not be able to wet the surface of the given substrate. Zisman was able to measure γ_c of many surfaces by measuring the changes in contact angles of different selected liquid that were applied to the surface. All these liquids he used for his measurements already had known predetermined surface tensions. Therefore, the critical surface tension could be determined.



Solid Contact Angle

Figure 2.3 Contact angle between solid adherend and liquid adhesive

As the contact angle approaches zero, the drop will cover a larger and larger area. When $\phi = 0$, complete spreading of the liquid has occurred across the surfaces. Therefore, ϕ is inversely a measure of wettability.

2.1.1.3 Solubility Parameter

Another method of measuring compatibility is by using Hildebrand solubility parameters. This solubility parameter is equal to the square root of the cohesive energy density (internal pressure) as shown below:

$$\delta = (\Delta E/V)^{1/2} \quad (2.2)$$

where δ = Solubility parameter

ΔE = Change in energy of vaporization

V = Molar volume

The energy of vaporization cannot be measured directly for polymers because they are obviously non-volatile. Therefore, indirect methods must be used to measure the solubility parameter of polymers. These values can be calculated, but the most common method is to simply compare the solubility properties of a given polymer to different selected solvents of known values in order to find the best solubility. A strong positive correlation has been reported between the critical surface tension (γ_c) and the Hildebrand solubility parameter (δ) for a wide range of different selected polymers. Although this

correlation is by no means perfect, it does show that both γ_c or δ can be used to help predict the compatibility of an adhesive with selected adherend.

In general, different solids have different specific surface free energy (ergs/cm²). Solids with strong intermolecular forces such as carbides, metal oxides, metals, etc., have high energy surfaces. On the other hand, very low melting organic solids of weak intermolecular forces have low energy surfaces. Glasses and some salts are considered intermediate. Lastly, most all liquids are considered to have low energy surfaces. Therefore, liquids generally will easily spread over the high energy surface solids.

Table 2.1 compiled from the work of Hildebrand and Scott, Small and Burrell, and other lists the solubility parameters of a number of adhesive and adhesive materials, along with a qualitative characterization of their crystallinity and molecule, and solubility parameters of various solvents.

2.1.2 Raw Materials for Adhesives

2.1.2.1 Base Polymers [15]

Almost every polymer and resin are used for the production of adhesives, it may be classified according to origin as:

- (1) Natural : starch, dextrans, asphalt, animal and vegetable proteins, natural rubber, shellac.

Table 2.1 Solubility Parameter

Polymer	Solubility parameter (cal/cm ³) ^{1/2}
Natural rubber	7.9-8.3
Toluene	8.9
Cellulose	10.3-11.5
Phenolic	11.5
Nylons	12.7-13.6

(2) Semi-synthetic : cellulose nitrate and the other cellulosics, polyamides derived from dimer acids, castor-oil based polyurthanes

(3) Synthetics :

(a) vinyl-type addition polymers, both resins and elastomer : polyvinyl acetate, polyvinyl alcohol, acrylics, unsaturated polyesters, NBR, SBR, neoprene, butyl rubber, polyisobutylene.

(b) Polymers formed by condensation and other step wise mechanisms : epoxies, polyurethanes, polysulfide rubbers, and the reaction products of formaldehyde with phenol, resorcinol, urea, and metamine.

2.1.2.2 Tackifiers [10, 14]

Tack is the bond strength that is formed immediately when a given material comes in contact with another surface. It has been called "instantaneous adhesion" after which bonding strength may rise to a higher level later in time.

Many elastomers and thermoplastic polymers have very poor inherent tack properties. In order to improve this tack quality, tackifying resins are added to most of these adhesive formulations including evaporation types, pressure sensitive types, and hot melts.

The addition of tackifiers can improve performance of a polymeric adhesive in several ways. First of all, the proper selection and loading of a given tackifying resin can improve the compatibility of a given polymer to a selected substrate. Another way that tackifying resins improve adhesion is through improving the wetting power by changing the viscoelastic properties of the polymer, so there is more plastic and less elastic behavior. This allows closer contact of polymer to substrate. Lastly, tackifying resins improve the tack properties (initial stick) of the adhesive to the substrate which leads to a stronger permanent bond later.

Tackifier examples are rosins, hydrocarbon resins, indene, coumarone, phenolic and polyterpenes.

2.1.2.3 Solvents [10, 14]

Solvents are used as carriers in evaporation type adhesives in which the base adhesive polymer is dissolved in the solvent to provide a liquid solution that will wet the adherend surface. After application, the solvent escapes from the glue line through evaporation leaving the polymer with good cohesion bonding strength.

Hildebrand solubility parameters are used to measure the compatibility of two substances such as a base polymer and a given substrate (section 2.1.1.3). In similar manner, Hildebrand solubility parameters can also be used in predicting the solubility of a given base polymer in a selected solvent. Generally, it has been found that solvents with similar chemical structures to the solute will dissolve the solute. In other words "likes dissolves liked".

2.1.2.4 Fillers [10, 14]

Fillers are important not only because they reduce the material cost of adhesives, but help reinforce the glue line formed, thus improving the cohesive strength of the adhesive. Also fillers help reduce contraction of the glue line in some case, thus providing a stronger bond with reactive polymer adhesive systems that form a hard rigid bond, the role of fillers in reducing shrinkage on hardening is far more important than any improvement in adhesive strength. Reducing shrinkage helps reduce any stress formation along the glue line thus providing for a stronger bond.

Preferred fillers are pyrogenic and precipitated silicas, chalks, talc, sand, wood flour and light and heavy spar although fibers and metal powders are used also.

2.1.2.5 Plasticizers [10, 14]

Plasticizers are used extensively in elastomer adhesives and hot melts. The main purpose of any plasticizer, as the name implies, is to aid in processing or breaking down the elastomer on the mill in order to effectively achieve a higher state of mix on the mill and enable the milled compound to be solubilized more readily by a given solvent. However, plasticizers not only improve processing, but many times have the side advantage of improving tack, just as some tackifiers also improve rubber processing.

Plasticizers, also affect adhesive use by reducing "drawing", reducing solution viscosities, improving low temperature flexibility of the glue line, and reducing modulus and hardness of the glue line.

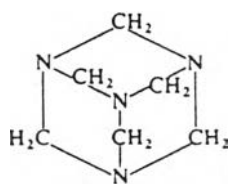
Phthalate plasticizers are the most widely used. Citric acid esters and glycerol triacetate are less important.

2.1.2.6 Hardeners [14]

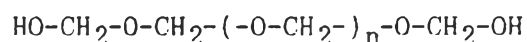
A hardener is used in reactive polymer adhesive systems to initiate the hardening of the glue line by initiating crosslinking or gelling within the polymer adhesive.

For phenol-formaldehyde novolac resins, the amount of formaldehyde reactant was held back in order to prevent the resin from reaching gel point and forming a three dimensional matrix. Upon the addition of a methylene doner (added in powder form to the cooled ground up resin), the novolac resin is able to gel when reheated. The methylene doner commonly used is hexamethylenetetramine or hexamine (I).

In a similar chemistry, paraformaldehyde (II) is used as the powder hardening agent (methylene donor) with novolac resorcinol-formaldehyde resin (usually in a liquid form) in order to cure the resins.



(I)



(II)

2.1.2.7 Primers [14]

A primer is a coating which is applied to a given adherend before the adhesive in order to improve the adhesive bond. Adhesives are not always compatible with a given substrate. A primer may be intermediate in its compatibility between a given adhesive and substrate or the primer may contain a compound with bifunctionality. Depending on what diversity of materials are being bonded, they can consist of epoxides, polyurethanes, polyisocyanates, methacrylates, silanes, or variety of resins.

2.1.2.8 Thickening Agents [14]

Some components are added to adhesive formulations in order to increase their viscosity, thickeners. Synthetic polymers can also be added to aqueous systems as thickeners. Soluble synthetic polymers such as polyvinyl alcohol or methyl cellulose can be used for this purpose. Bentonite also is used as an aqueous thickener because of its gel forming tendency.

2.1.3 Classification of Adhesives [14, 15]

2.1.3.1 Chemically Reactive Types

The chemically reactive types of adhesives usually involve the polymerization of low molecular weight liquid components upon application to form a polymerized glue line which will have good cohesive strength. There are two basic types of chemically reactive adhesives. One type consists of those reactive adhesives which give off a low molecular weight by-product (usually water) during a polymer condensation reaction. Examples of this type are the phenol-formaldehyde and resorcinol-formaldehyde adhesives. The other type of reactive adhesive polymerizes without the formation of a low molecular weight by-product sometimes through addition polymerization. Examples of this type are epoxies, cyanoacrylates, urethanes, and polyesters.

2.1.3.2 Evaporation Types

Evaporation type adhesives consist of a polymeric material being carried in a liquid state by a liquid

carrier whether it is as an aqueous colloidal dispersion (latex) or as a solution in an organic solvent. Of course after application, the liquid carrier must be lost by evaporation or by diffusion into a porous substrate in order to obtain a solid glue line and good cohesive strength. The organic solution adhesives are faster drying than the latex adhesives; on the other hand, for the glue line to have good cohesive strength may require a higher molecular weight polymer.

2.1.3.3 Hot Melt Types

It consists of thermoplastic polymer and usually other additives. This adhesive when applied hot (above melting) to a given substrate, effectively wets the surface; however, on cooling, the molten polymer returns to its solid form providing good cohesive strength to the bond. The advantage to hot melt adhesive types is that they set very quickly after applied.

2.1.3.4 Pressure Sensitive Types

In the case of a pressure sensitive adhesive, the physical transformation, the liquid state is converted into a solid form, does not occur. A pressure sensitive adhesive is, in a way, both in the liquid stage (for wetting) and in the solid stage (for cohesive strength) at the same time. It consists of a viscoelastic material which is fluid enough to wet a surface under a slight applied external pressure, yet cohesive enough to provide some moderate strength in holding the adherends



together after external pressure is released. Typically, these pressure sensitive adhesives are based on various elastomers which have been made sticky with the use of resin additives. The application in providing adhesion for tape and labels are well known. One obvious disadvantage is its relatively poor cohesive strength compared to other adhesive types.

2.1.4 Mechanisms of Adhesion [10, 11, 16]

The attainment of intimate molecular contact at the adhesive/substrate interface is invariably a necessary first stage in the formation of strong and stable adhesive joints. The next stage is the generation of intrinsic adhesion forces across the interface, and the nature and magnitude of such forces are extremely important. They must be sufficiently strong and stable to ensure that the interface does not act as the "weak link" in the joint, either where the joint is initially made or throughout its subsequent service life. The various types of intrinsic forces which may operate across the adhesive/substrate interface are commonly referred to as the *mechanisms of adhesion*. There are four main mechanisms of adhesion, namely:

- (a) Mechanical interlocking,
- (b) Diffusion theory,
- (c) Electronic theory,
- (d) Adsorption theory.

The molecular forces in the surface layers of the adhesive and substrate greatly influence the attainment of intimate molecular contact across the interface and such molecular forces are now

frequently the main mechanism of adhesion, the adsorption theory.

2.1.4.1 Mechanical Interlocking

The oldest theory of adhesion is definitely the mechanical theory. It is based on mechanical anchorage of the adhesive in pores and irregularities in the substrate surface, adherend and is discussed primarily in reference to wood and similar porous material.

The mechanical interlocking is the major source of intrinsic adhesion in roughness surface substrate. There is much work to be found in the literature which convincingly demonstrates that increasing the surface roughness of the substrate may increase the measured strength of the adhesive joint.

2.1.4.2 Diffusion Theory

The diffusion theory of adhesion is essential applicable to the bonding of high polymers. Voyoskii [16]) is the chief advocate of the diffusion theory of adhesion which states that the intrinsic adhesion of polymers to themselves (autohesion), and to each other, is due to mutual diffusion of polymer molecules across the interface. This requires that the macromolecules or chain segments of the polymers (adhesive and substrate) possess sufficient mobility and are mutually soluble. This latter requirement may be restated by the condition that they possess similar values of solubility parameter. Hence, the solubility parameter is an index of the

compatibility of two components, e.g., if an amorphous polymer and a solvent have similar values of solubility parameter then they should form a solution.

2.1.4.3 Electronic Theory

If the adhesive and substrate have different electronic band structures there is likely to be some electron transfer on contact to balance Fermi levels which will result in the formation of a double layer of electrical charge at the interface. Deryaguin and co-workers [16] have suggested that the electrostatic forces arising from such contact or junction potentials may contribute significantly to the intrinsic adhesion.

2.1.4.4 Adsorption Theory

The adsorption theory of adhesion is the most widely applicable theory and proposes that, provided sufficiently intimate molecular contact is achieved at the interface, the materials will adhere because of the interatomic and intermolecular forces which are established between the atoms and molecules in the surfaces of the adhesive and substrate. The most common such forces are van der Waals forces and these are referred to as secondary bonds. Also, it may be included hydrogen bonds. In addition, chemical bonds may sometimes be formed across the interface. This is termed chemisorption and involves ionic, covalent or metallic interfacial bonds being established; these types of bonds are referred to as primary bonds. Also, it has

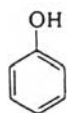
been proposed that donor-acceptor interactions may occur across an interface and these are typically intermediate in strength between secondary and primary bonds.

Good adhesion can be expected if the adhesive (in liquid form or in a liquid medium) wets the substrate .

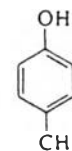
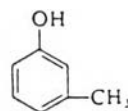
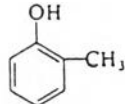
2.2 Phenolic Resins

2.2.1 Introduction [7, 9, 17, 18]

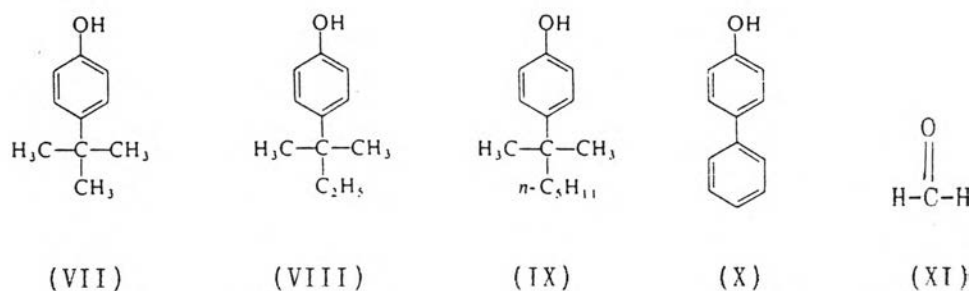
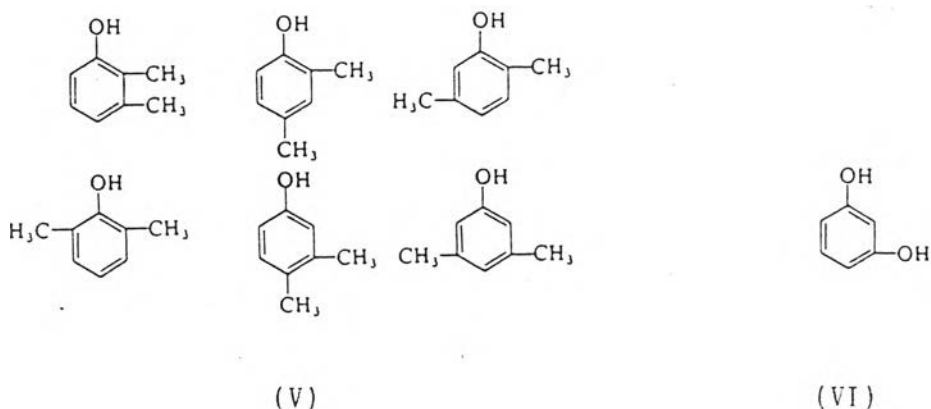
Phenolic resin (phenol-aldehyde polymer) are polymers formed by the interaction of a phenol and/or substituted phenol and aldehyde with strong acid or alkaline catalysts. The phenols of commercial importance are phenol (III) itself, cresols (IV), xylenols (V), resorcinol (VI) and higher homologues of phenol, i.e., para-tertiary-butyl phenol (VII), p-tert-amyl phenol (VIII), p-tert-octyl phenol (IX), and p-phenyl phenol (X) ; also, a product derived from Cashew Nut Shell Liquid (CNSL), which is a mixture of phenol derivatives (scheme 1.1). It may be noted that several aldehydes other than formaldehyde (XI) have been used to prepare phenolic polymers but none has attained appreciable commercial significance .



(III)



(IV)



Phenolic resins find practical utilization mainly in the form of network polymer. The polymerization is normally carried out in two separate operations. The first operation involves the formation of a low molecular weight fusible, soluble resin, and the second operation involves curing reactions which lead to the cross-linked product. Various types of initial low molecular weight resin are produced commercially, resol and novolak resins.

The thermosetting (i.e., nonsubstituted) phenolic resins are employed as structural adhesives for laminating, and for bonding applications: bonded and coated abrasives, friction materials, fiber bonding, foundry use, and wood bonding.

The resins based on para substituted phenols are not capable of crosslinking to a thermoset state. These resins

are employed as tackifiers in contact, pressure sensitive, and hot-melt adhesives.

The meta substituted isomer is tri-functional, and, therefore, crosslinking will occur. Substituted phenols provide improved compatibility with rubbers (in adhesives) and drying oils (in varnishes).

2.2.2 Factors Influencing the Course and Speed of The Reaction [7, 9, 18]

Precise control of the course, speed, and extent of the reaction is essential for the manufacture of products. Factors important for achieving this control are:

1. The choice of phenols.
2. The phenol:formaldehyde molar ratio.
3. The type and amount of catalyst, including pH of reaction mixture.
4. The time and temperature of reaction.

The phenol:formaldehyde molar ratio, coupled with the type of catalyst use, determine whether the polymer will be phenol terminated or methylol, $-CH_2OH$, terminated. If phenol terminated, the resin is referred to as a novolak or a two-step resin. Such a resin is not heat-reactive until a second ingredient is added that supplies the formaldehyde needed to effect cure. The most widely used curing agent is hexamethylenetetramine (I). If methylol terminated, the resin is referred to as a resol or a one-step resin. This type is heat-reactive.

In both resols and novolaks, the resinous state is due to the presence of isomers and of homologous products with a wide range of molecular size, rather than to the presence of large molecules such as are found in most of the ethenoid polymers.

2.2.3 Resol Resins (One-Step Resins) [17,18]

Resol resins are prepared by the interaction of a phenol with a molar excess of formaldehyde (commonly about 1 : 1.5-2) in the presence of an alkaline catalyst. Common alkaline catalysts are NaOH, Ca(OH)₂, and Ba(OH)₂. This excess may be small or large according to the type of resin required [7]). It should be noted that resols can not normally be made from the higher aldehyde. The molecules contains reactive methylol groups, heating causes the reactive resol molecules to condense together to form larger molecules, a result achieved without the addition of a substance containing reactive methylene (or substituted methylene) groups.

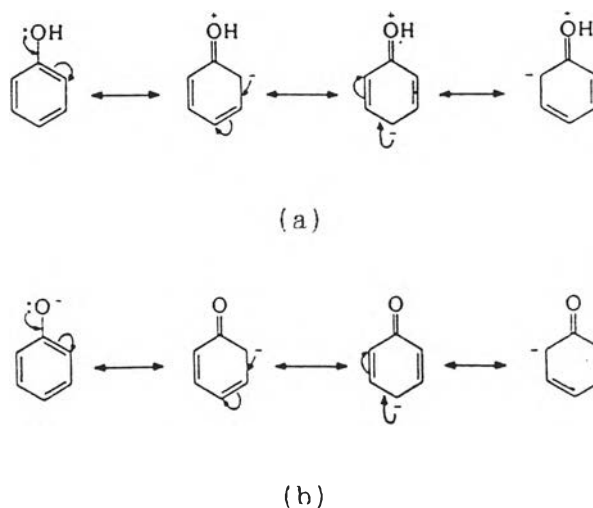
Curable phenol-formaldehyde resins of the resol type are of considerable importance as hot-setting reactive adhesives for bonding wood and metals.

2.2.3.1 Mechanism and Preparation [7, 17]

The reaction in making resols consists of an initial addition reaction between the phenol and formaldehyde to form phenol-alcohols (XII, XIII), follow by a condensation reaction of these , either with one another or with

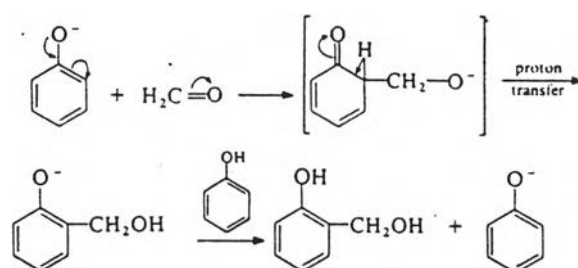
more phenol, and then in turn by successive further addition and condensation reactions.

In undissociated phenol, delocalization of an unshared electron pair on the oxygen atom results in increased electron densities at the o- and p-positions. This effect is larger than the decrease in electron density which results from the inductive effect of the hydroxyl group (scheme 2.1 a). Thus substituted of phenol by electrophilic reagent takes places at the o- and p-positions. In the phenoxide ion, similar delocalization occurs but because of the negative charge on the oxygen atom the inductive effect is greatly increased and reversed in direction so that electron density in the benzene ring is notably increased (scheme 2.1 b). Thus phenol is more reactive and more o-/p-directing in alkaine solution than in neutral or acid solution.



Scheme 2.1 Resonance of phenol (a) and phenoxide ion (b)

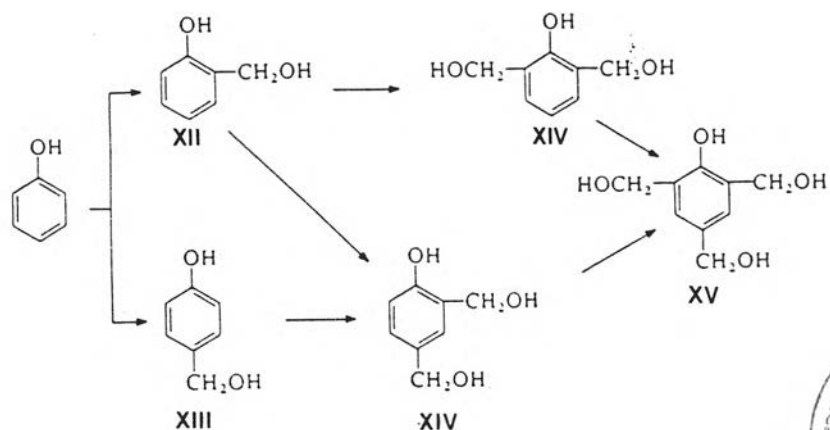
The reaction of phenol and formaldehyde in alkaline conditions therefore results in the formation of o- and p-methylol groups, scheme 2.2. (It should be noted, however, that the identity of the actual hydroxyalkylating species has not been established and it is not clear how formaldehyde, as methylene glycol, reacts with the phenoxide ion.) The resulting o- (XII) and p-methylolphenols (XIII) are more reactive towards



Scheme 2.2 Formation of o-methylolphenol

formaldehyde than the original phenol and rapidly undergo further substitution with the formation of di- (XIV) and trimethylol derivatives (XV). Since virtually no substitution occurs at the m-position, the possible products are as shown in scheme 2.3. All of these compounds have been obtained from aqueous alkaline solutions of phenol and formaldehyde.

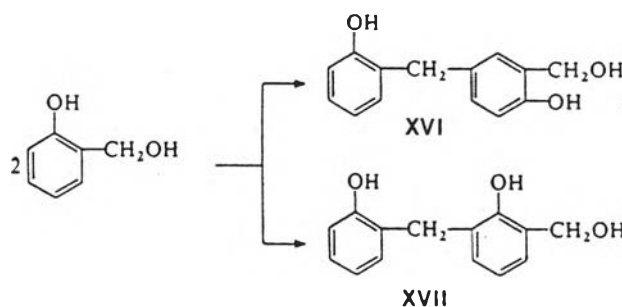
The methylolphenols obtained are relatively stable in the presence of alkali but can undergo self-condensation to form dinuclear and polynuclear phenols in which the phenolic nuclei are linked by methylene groups. These products can arise from two different types of self-condensation; one involves two methylol groups and the other involves a



Scheme 2.3 Formation of di- and tri-methylolphenol

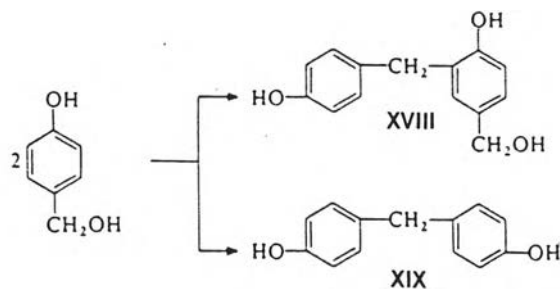


methylolphenol. Examples of such reactions are provided by an investigation in which *o*- and *p*-methylolphenols were heated with aqueous sodium hydroxide at 80 °C and the products analysed by paper chromatography. *o*-Methylolphenol gave 3-methylol-2',4'-dihydroxydiphenylmethane (XVI) by reaction between a methylol group and a *p*-hydrogen atom together with traces of 3-methylol-2,2'-dihydroxydiphenylmethane (XVII) by reaction between a methylol group and an *o*-hydrogen atom, scheme 2.4.



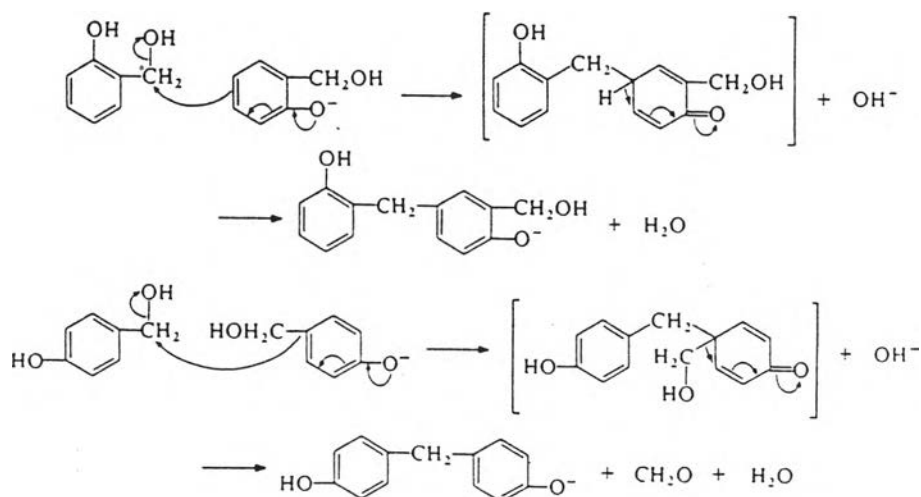
Scheme 2.4 Self - condensation of *o*-methylolphenols yield dinuclear phenols

p-Methylolphenol gave 5-methylol-2,4'-dihydroxydiphenylmethane (XVIII) by reaction between a methylol group and an o-hydrogen atom and 4,4'-dihydroxydiphenylmethane (XIX) by reaction between two methylol groups, scheme 2.5.



Scheme 2.5 Self-condensation of p-methylolphenols

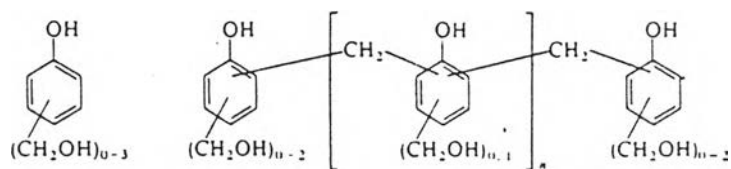
Possible mechanisms of these two types of self-condensation are shown below, scheme 2.6. Both cases involve attack on a methylol group with displacement of a hydroxyl group. In the first case a proton is subsequently eliminated and in the other a methylol group is subsequently eliminated (as



Scheme 2.6 Possible self-condensation mechanism of o- and p-methylolphenols

formaldehyde). Which of these two types of reactions occurs in any particular case depends on the experimental conditions and the structure of the methylolphenols involved. Generally, p-hydrogen atoms and p-methylol groups are the predominant sites for the self-condensation of methylolphenols.

The above reactions, which are shown as leading to dinuclear phenols, may be repeated so that trinuclear phenols are formed, and so on. Thus the product obtained by the reaction of phenol and formaldehyde under alkaline conditions is a complex mixture of mono- and polynuclear phenols in which the phenolic nuclei are linked by methylene groups. The structures of the components of such a mixture may be represented as follow in scheme 2.7:



Scheme 2.7 Mono- and poly-nuclear phenols

In these general formulae, the methylol groups and methylene bridges are restricted to o- and p-positions and there is a tendency for o-methylol groups and p-methylene bridges to predominate. Typical commercial liquid resols have an average of less than 2 aromatic rings per molecule whilst solid resols have 3-4.

It may be noted that the conversion of resol molecules into high molecular weight, cross-linked materials may be accomplished by simply heating a resol, it being unnecessary to add any further reagent. The preparation of resols is often referred to as a "one-stage" process, since a quantity of formaldehyde sufficient to permit the formation of highly cross-linked material is present from the outset. Thus during the preparation of a resol, polymerization is steadily advancing and there is a danger of gelation in the reactor of reaction is taken too far.

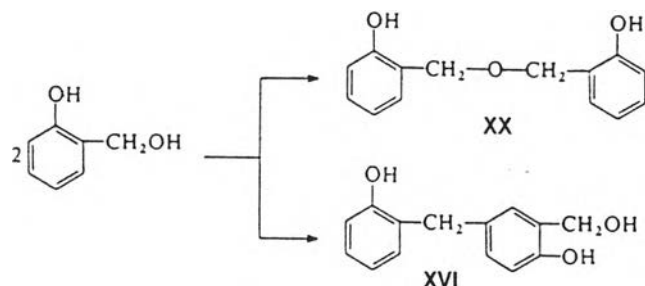
2.2.3.2 Cross-Linking of Resol Resin [17]

Resols, which are produced under alkaline conditions, are generally neutralized or made slightly acid before curing is carried out. Network polymers are then obtained simply by heating.

The curing of resol is extremely, involving a number of competing reactions each of which may be influenced by reaction conditions it is easy to unravel precisely what takes place. Also, the cured product, being infusible and insoluble, is not amenable to chemical investigation.

When pure (i.e. neutral) o-methylolphenol is heated at 110 °C the main product is 2,2'-dihydroxydibenzyl-ether (salireton, XX) with very little of the methylene compound (XVI), scheme 2.8. It was also found in this investigation that when o-methylolphenol is heated at 70 °C in the presence of hydrochloric acid both compounds (XX) and (XVI) are produced

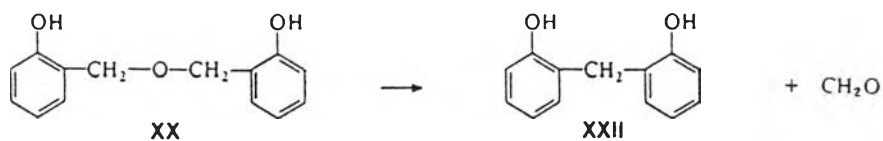
but in the presence of sodium hydroxide only the methylene compound (XVI) is formed. Thus when a resol is cured, it is likely that both methylene and ether links are present in the product.



Scheme 2.8 Self-condensation of o-methylolphenol at 110°C

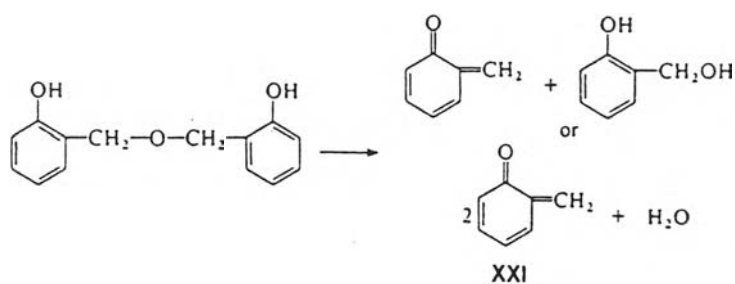
It was found that whilst methylene compounds are generally rather stable, dibenzyl ethers are not so stable and at temperature above about 150°C (i.e. at temperature commonly used for curing resol) they undergo a number of ill-defined reactions. The mechanisms of these secondary reactions have been extensively studied but are still rather poorly understood.

Zinke and his co-workers have postulated that the main reaction involve is the breakdown of ether links to give methylene links with loss of formaldehyde, scheme 2.9. To account for the fact that less than one mole of formaldehyde is evolved for each ether link broken it is supposed that some of the formaldehyde produced reacts with the methylene compound, resulting in cross-linking.

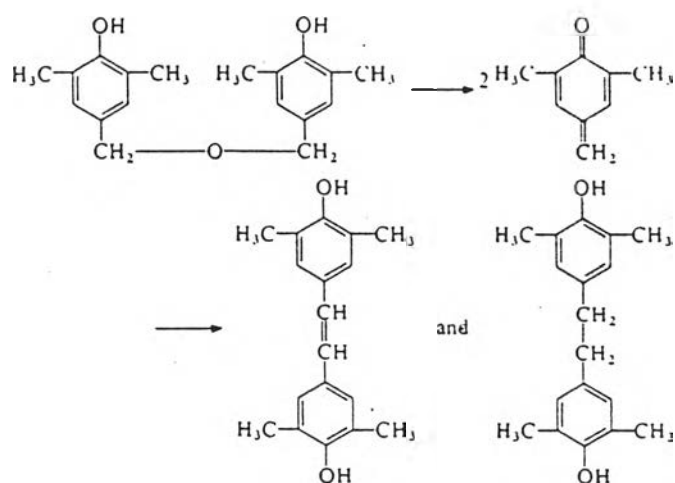


Scheme 2.9 Breakdown of ether linkage

On the other hand, Hultzsch and Euler and co-workers have suggested that the main reaction involved in the breakdown of ether links is the formation of quinone methides (XXI) e.g., scheme 2.10:



Scheme 2.10 Formation of quinone methides.



Scheme 2.11 Formation of stilbene and diphenylethane

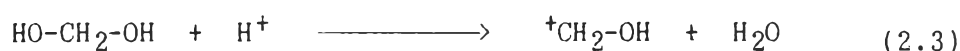
It may be mentioned that it is common practice to refer to resols as "A stage resins" and to the final network polymers as resites or "C stage resins" ; intermediate materials are called resitols or "B stage resins".

2.2.4 Novolak resins [17]

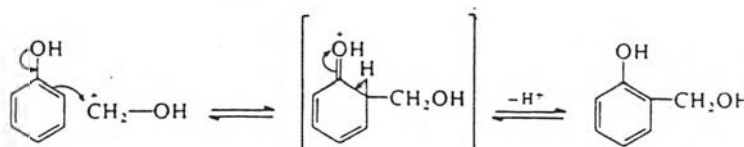
2.2.4.1 Mechanism

Novolak resins (novolaks or novolacs) are normally prepared by the interaction of a molar excess of phenol with formaldehyde (commonly about 1.25 : 1) under acidic conditions.

The reaction between phenol and formaldehyde under acidic conditions proceeds through a mechanism different from that describe previously for the base-catalyzed reaction. The initial step involves the protonation of formaldehyde (methylene glycol) to give carbenium ion:

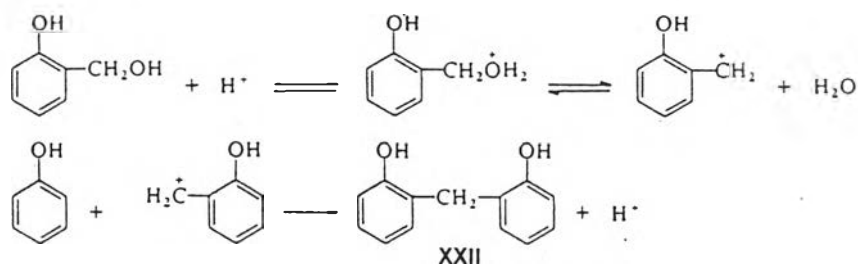


The phenol then undergoes electrophilic substitution with the formation of o- and p-methylol groups, e.g, scheme 2.13:



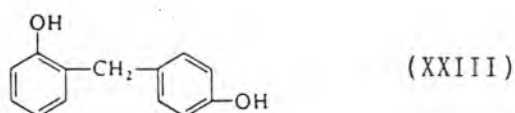
Scheme 2.13 Electrophilic substitution of phenol in acid-catalyzed reaction

In the presence of acid the initial products, o- and p-methylolphenols, are present only transiently in very small concentration. They are converted to benzylic carbenium ions which rapidly react with free phenol to form dihydroxydiphenylmethanes, e.g., scheme 2.14:



Scheme 2.14 Formation of dihydroxydiphenylmethane

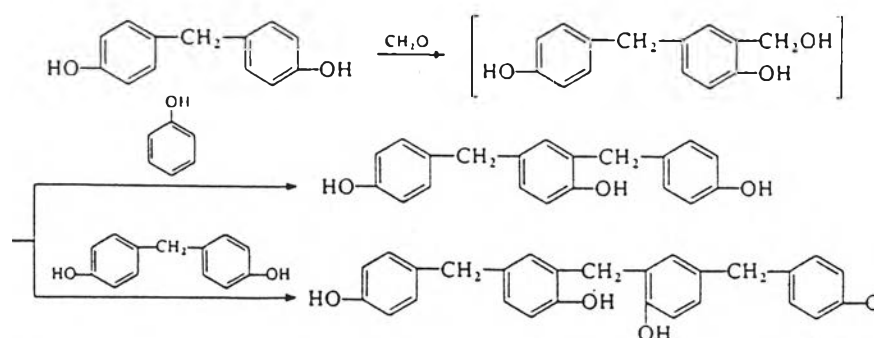
Since the phenol does not undergo substitution at m-position, there are possible three dihydroxydiphenylmethane, namely 2,2'- (XXII), 2,4'- (XXIII) and 4,4'-dihydroxydiphenylmethane (XIX).



The proportions in which the three isomers are formed depend on the condition used, particularly on pH. Under strongly acidic conditions (below pH 2), such as are normally used in making novolaks, only the 2,4'- and 4,4'-isomer were isolated in any appreciable yield whereas at a higher pH(3-6) the 2,2'-isomer predominated. In the acid-catalyzed reaction between phenol and formaldehyde the first substitution in the phenolic nucleus substantially deactivates the ring against further substitution

(in contrast to the base-catalyzed reaction). Also, although the dihydroxydiphenylmethanes formed are activated in the same manner as the single phenolic nucleus, the activation is not so strong. Because of the aforementioned factors, there is an initial build-up in the concentration of dihydroxydiphenylmethanes.

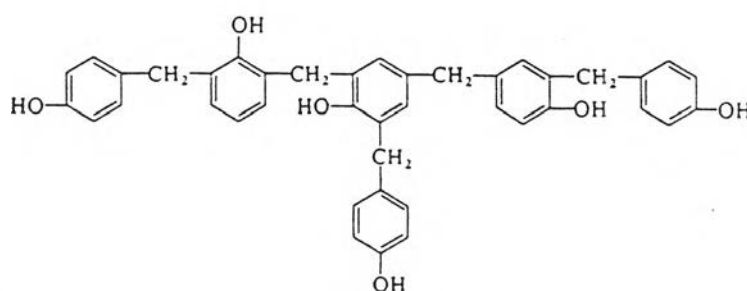
The concentration of dihydroxydiphenylmethanes subsequently falls as polynuclear phenols are produced by further methylation and methylene link formation, e.g., scheme 2.15:



Scheme 2.15 Formation of polynuclear phenols

Reaction of the below type continue until all the formaldehyde has been consumed. The final product therefore consist of a complex mixture of polynuclear phenol linked by o- and p-methylene groups. The average molecular weight which is eventually attained is governed by the initial molar ratio of phenol and formaldehyde. The average molecular weight (M_n) of a typical commercial novolak is about 600, which corresponds to about six phenolic nuclei per chain; the number of nuclei in individual chains is typically in the range 2-13. The

potentially reactive third positions in the nuclei of a novolak are deactivated and thus the chains are essentially linear, although a small amount of branching occurs. The complexity of novolaks is illustrated by the fact that for a chain of eight phenolic nuclei there are 1485 possible unbranched isomers and around 11000 branched isomers. A typical novolak chain might be represented as follows in scheme 2.16.



Scheme 2.16 A typical novolak resin

The essential feature of novolaks is that they represent a completed reaction and themselves have no ability to continue increasing in average molecular weight. The resins are therefore permanently fusible and there is no danger of gelation during production. This is in contrast to resols which contain reactive methylol groups and are capable of cross-linking on heating. In order to convert novolaks into network polymers the addition of an auxiliary chemical cross-linking agent is necessary. Because of this requirement, the preparation of novolaks is often referred to as a "two-stage" process.

In conclusion, it may be noted that novolaks can be prepared using mildly acidic catalysts such as zinc acetate. The resulting products have a high proportion of o-o'-links and are commonly called "high-ortho novolaks". Such novolaks are more reactive than the normal resins and are sometimes preferred.

2.2.4.2 Cross-Linking of Novolak Resin

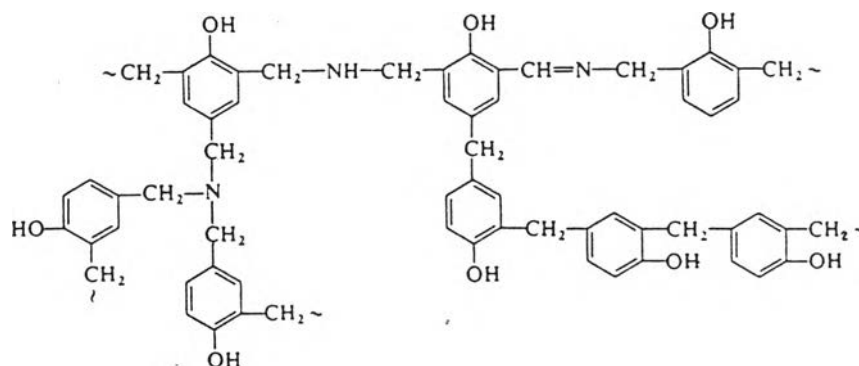
As noted previously, the conversion of novolaks into network polymers can be accomplished only after the addition of a cross-linking agent. Although novolaks can be cross-linked by reaction with additional formaldehyde or with paraformaldehyde, hexamethylenetetramine is almost invariably used for this purpose. The mechanism of the curing process is not fully understood.

The primary reaction between a novolak and hexamethylenetetramine (which in a typical commercial moulding powder is present to the extent of only about 12% on the weight of resin) leads to a complex structure containing secondary and tertiary amine links. On further heating most of these links break down to give methylene links and the resulting product has only a small nitrogen content. Some azomethine links may be formed and may account for the characteristic brown colour of the cured material.

A study of the novolak-hexamethylenetetramine reaction by differential thermal analysis and thermogravimetric analysis supports the view that the cross-

linking reaction proceeds through dibenzylamines.

To summarize, it may be said that the network polymer obtained from a hexamethylenetetramine-cured novolak is composed of phenolic nuclei joined mainly by methylene groups with small numbers of various nitrogen-containing links. The possible structure of such a network might be represented as follows in scheme 2.17:



Scheme 2.17 Possible structure of network novolak resin

It is to be noted that the relative amounts of the various linkages shown above are not intended to have any quantitative significance. Thus the network polymer obtained from the novolak-hexamethylenetetramine reaction has a structure which is predominantly similar to that of the network polymer derived from a resol.

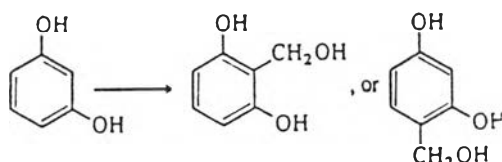
2.3 Resorcinol- Formaldehyde Adhesive

2.3.1 Introduction [19]

Resorcinol (VI), like ordinary phenol is tri-functional in its reaction with formaldehyde, but having a second hydroxyl group in the meta-position. It is more powerfully directing in the para- and ortho-positions. The reactivity is such that equimolecular proportions of resorcinol and formaldehyde will react by themselves at room temperature to produce a gel. Such one-stage resins are, however, of small practical worth as adhesives, and so commercial resorcinol glues are two-stage resins: the first stage is carried out by the manufacturer in forming the novolak, and the second stage is carried out by the user in converting the novolak to a resite by adding formaldehyde.

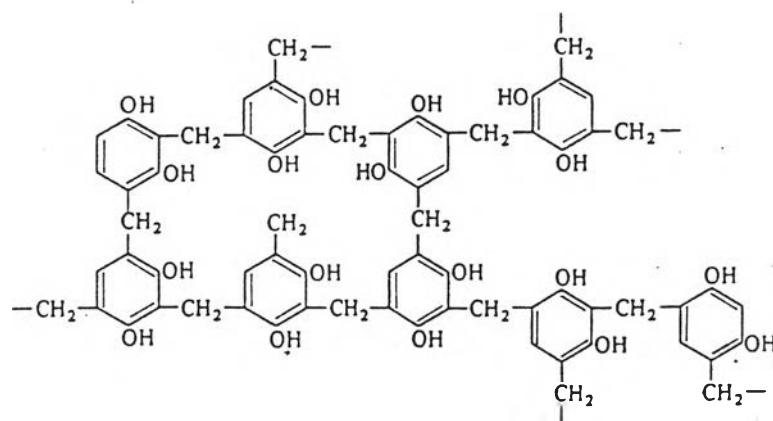
2.3.2 Chemistry and Resin Formation [20]

Resorcinol is similar to phenol in that it readily combines with formaldehyde to form methylol derivatives, with the methylol groups occupying either the positions ortho to both hydroxyl groups, or ortho to one and para to the meta position is not ordinary reacted, as shown in scheme 2.18.



Scheme 2.18 Condensation product between resorcinol and formaldehyde

The reactivity of these methylol derivatives is so high, they cannot easily be isolated in pure stable form. They continue to react under ambient, uncatalyzed conditions with formaldehyde, resorcinol or other methylol-containing molecules to form polymer chains of higher molecular size, with branched, as well as linear, configurations of great complexity. These reactions continue until spatial considerations prevent further interaction. In these polymers the resorcinol nuclei are joined together through methylene linkage to give complex molecules such as may be shown schematically as follow in scheme 2.19:



Scheme 2.19 Complex molecule of resorcinol-formaldehyde resin

Thus, resorcinolic resins, regardless of catalyst used, do not exist as resoles, as phenolics do, but are similar to the novolaks which result when phenol and formaldehyde are combined in the presence of acidic catalysts. That is, all of the resorcinol nuclei are linked together through methylene bridges with no detectable ether formation. Methylol groups appear to exist only in very dilute solutions.

Since the introduction of a methylol group onto the ring increases the activity of the other nuclear positions, it is readily apparent why resorcinol resins have so great a tendency to continue to react as long as there are active sites available.

An important application of a resorcinol resin is in improving the adhesion of rubber to rayon and other synthetic fibers [19]

2.4 Linseed Oil [21, 22]

Linseed oil, highly unsaturated oils, is obtained from the seeds of the flax plant, Linum usitatissimum, which is indigenous to central Asia. The plant is now cultivated throughout the Temperate Zone. The oil content of the seeds is 33-43 per cent. Exposed to air, it is oxidized and convert into an elastic solid known as "linoxyn".

Crude linseed oil has a dark amber color and a stronger characteristic odor. The odor of linseed oil appears to be associated to a large extent with the highly unsaturated acids of the oil and is inclined to reoccur after the oil has been steam deodorized. The color of linseed oil can be reduce to a pale yellow, similar to that of other refined vegetable oils, by suitable refining and bleaching treatment.

The characteristics and fatty acid composition of a number of linseed oils from various sources that were reported during the perios 1943-1949 are in table 2.2.

Table 2. Characteristics and composition of linseed oils of various iodine numbers reported during the period 1943-1949

Analysis	North American (450)	North American (451)	Argentinian (452)	North American (452)	Range of Values
Characteristic					
Iodine number	164.8	189.1	176	202.8	165-204
Refractive index at 25°C	—	—	—	—	1.477-1.482
Titer, °C	—	—	—	—	19-21
Unsaponifiable matter, %	0.94	—	—	0.91	Not over 1.7%
Fatty acids, wt. %					
Palmitic	—	—	—	—	4-7
Stearic	—	—	—	—	2-5
Arachidic	—	—	—	—	0.3-1
Total saturated	11.8	8.7	16.5	7.3	—
Oleic	26.4	24.1	15.4	14.2	12-34
Linoleic	22.2	17.4	15.2	16.7	17-24
Linolenic	39.6	49.4	52.9	61.8	35-60
Total unsaturated	88.2	90.9	83.5	92.7	—

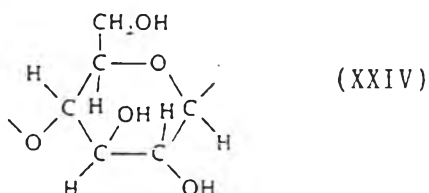
2.5 Wood [23, 24]

In many ways, wood, one of man's oldest and most widely used materials, resembles the polyblends or composites. Since wood is a mixture of two polymers, it is a polyblend. Its behavior, however, more closely resembles that of oriented fiber composites.

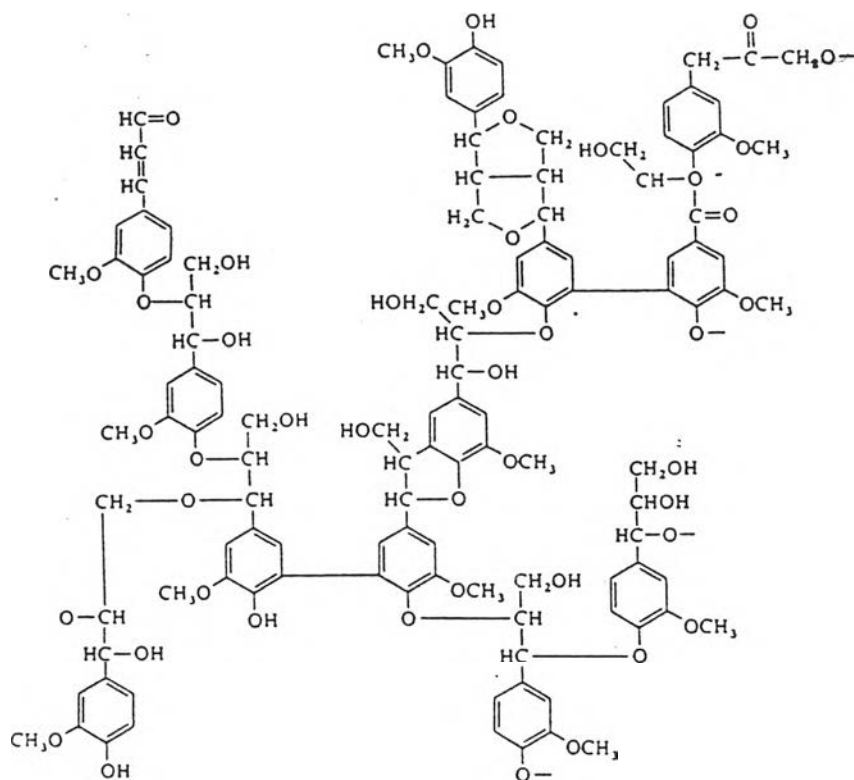
Wood contains two continuous phases: a cellular fibrous structure largely composed of cellulose, and a network of lignin, which serves as a bonding agent. In addition, depending on the degree of drying, either water or air is contained as a third phase within the lumen structure of the cells.

2.5.1 Chemistry

Cellulose is a linear, highly crystalline polymer having a polyglucoside structure (XXIV):



Lignin is a highly crosslinked amorphous polymer based on p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, and their phenolic glucoside. The structure of this highly irregular material is represented in scheme 2.20, in which possible crosslinking modes are illustrated.



Scheme 2.20 Summary of lignin structure. This natural thermoset plastic has a very irregular structure with various ether groups acting as crosslinks in many cases.

2.6 Literature Reviews

C.P. Dhamaney [25] explained the acid polymerize CNSL for plywood adhesives. They were prepared in an acid-catalyzed reaction of CNSL, in place of phenol. The adhesion of products, catalyzed by HCl, MnO₂ and HNO₃, maleic acid, and stearic acid was improved by the addition of CuCl₂ hardener, indicative of a 2-stage resin system. He found that oleic acid catalyst yield a 1-stage resin. The best 2-stage adhesive was prepared by using a 2% H₂SO₄-CuCl₂ mixture.

In 1970, Dhamaney [26] studied the plywood adhesive based on CNSL and urea. The mixtures of CNSL 90, urea 10 and formaldehyde 35 parts was refluxed 3 hr at 60-70°C in the presence of Ca(OH)₂, Na₂CO₃, or H₂SO₄ to give a product for bonding plywood which CuCl₂ and CuCO₃ were used as hardeners. Also, he described the adhesive preparation from gluten, CNSL and formaldehyde that it was suitable for the preparation of plywood, providing a use for gluten which was a starch industry waste [27].

In 1971, he explained about physical and chemical analysis of CNSL and correlation thereof with glue adhesion properties. CNSL was reacted with formaldehyde in alkaline catalyst to form a resin which had good glue adhesion when the CNSL contained \leq 0.015 % anacardic acid. Copper chloride and copper carbonate were used to induce crosslinking. He evaluated that good adhesion was due to unreacted side chains which were used to form a linear polymerization product, could soften at high temperature, resulting in a glue-like substances [28]. And

he prepared plywood adhesive, based on CNSL by treated it with \geq 35 parts of 40 % formaldehyde in the presence of alkaline catalyst and dissolved the resin in $\text{CHCl}_3 : \text{CCl}_4$ before applied to wood with CuCl_2 . An addition of 10 % phenol or xylenol to CNSL gave good adhesion [29].

Dhamaney [30] studied aniline formaldehyde resins in the field of CNSL based plywood adhesives. Aniline and formaldehyde were condensed in the presence of HCl and the resin was mixed with phenol or xylenol, formaldehyde, CNSL and an NH_3 catalyst and heat at $60-70^\circ\text{C}$. Phenol and xylenol improved the bonding quality of the resin. Adhesion was also improved by adding a CuCl_2 hardener, 2-stage resins.

In 1978, Dhamaney described the using of furfural in CNSL adhesives for plywood. CNSL was optionally mixed with approximately 10% phenol and furfural of furfural-formaldehyde mixtures in the presence of Cu compound hardeners which gave good adhesive bonds. Phenolic resins were prepared by both alkaline and acid catalysis, and the effects of various hardeners on the adhesive performance were determined [31]. Also, he evaluated the adhesion of CNSL-modified phenolic resin adhesives to rotary cut veneers in the presence of various catalysts and hardeners. All hardeners except Zn chromate, Pb chromate, Cu naphthenate and CuCO_3 behaved normally based on adhesive failure after 3 hr boiling. NaOH and COCl_2 catalyzed resins were 2-stage resins and the use of a hardener, e.g., CuCl_2 , improved the bond strength. PbCrO_4 catalyzed resin had poor bond strength even with hardener [32].

K. Sthapitanonda and others [33] explained the production of adhesive from Tapioca starch and CNSL on laboratory scale. Tapioca starch and CNSL when cross-link with formaldehyde in the presence of alkali yielded a high viscous dark brown adhesive. The mixture was heated about 1 hr at 95-97°C then thinned down with xylene and continued heated for 1 hr. After mixing with driers, the product became air-drying adhesive which was suitable for plywood.

