PREPARATION OF PHENOLIC RESINS FROM SASOL PHENOSOLVAN PITCH

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Andreas Stephanou

5 th day of APRIL 1991

ABSTRACT

Phenosolvan pitch from the SASOL 1 plant was used to develop exterior grade thermosetting adhesives for plywood and particleboard.

Phenosolvan pitch is a co–product obtained by SASOL in the petrol–from–coal process and it has a high content of phenolic compounds. The work involved in this research project was based on the idea of the utilization of these phenolic components to develop phenolic–type resins for exterior grade wood adhesives. Firstly, the reactivity of the phenosolvan pitch towards formaldehyde was investigated through pot life and gel time tests and the feasibility of the material to form thermosetting resins under alkaline conditions, i.e. resol–type of resins, was established. Based on the assumption that the 40% unknown fraction of the phenosolvan pitch consists of oligomeric material, the pitch was treated as an already made phenolic resin that can be cured by addition of paraformaldehyde as hardener. Condensation of the phenosolvan pitch with fortifiers such as wattle tannin extract and phenol–formaldehyde resins that act as cross–linking agents overcome the lack of strength which probably results from low degree of cross–linking in the unfortified phenosolvan pitch adhesive. Fully exterior marine grade plywood was produced by combining pure phenolic resin with SASOL 1 phenosolvan pitch at the 20/80 level. Small additions of commercial urea–formaldehyde resins can also be incorporated into the pitch–based adhesive without affecting the water resistance of the resin.

Samples from different batches of phenosolvan pitch vary considerably in both viscosity and reactivity. This inconsistancy, however, is not of a great concern because the high strength results obtained provide a broad safety margin. Other defects such as bleed–through and the characteristic tar odour of the phenosolvan pitch were greatly reduced after optimization of conditions of glue–mix preparation and application.

The pitch–based glue–mix is characterized by a short pot life which, although it allows application in a laboratory scale, it would most probably impose serious problems in the event of an industrial application. However, grafting the phenolic fortifier into the phenosolvan pitch and adding solvents such as water and methanol extend the pot life thus increasing the chances for a successful industrial application. The use of solvents also lowers the viscosity of the phenosolvan pitch rendering it usable as a particleboard adhesive. The particleboard results also appear quite promising but further improvement is necessary before they can meet the standard specifications.

A relative kinetic study on the reaction rates of pitch components with paraformaldehyde revealed that the reaction of monomethylolated phenols appears to be reduced by the presence of more highly reactive phenols whereas fast reacting phenols such as m–cresol do not appear to lose reactivity by interference. This study was based on infrared spectroscopy.

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CHAPTER ONE

1. LITERATURE REVIEW

Phenolic resins are a class of synthetic materials that have grown continuously in terms of volume and applications for over eight decades. The building blocks used in greatest volume are phenol and formaldehyde.

The early investigation of the reaction of phenol and formaldehyde began with the work of von Baeyer and others in the early 1870's as an extension of phenol–based dye chemistry. The initial experiments resulted in soluble, amorphous products whose properties elicited little interest. In 1899, the first patent for a phenolic–resin product intended for use as a hard–rubber substitute was granted. The first commercial product was introduced as a shellac substitute in the early 1900's.

However, although phenolic resins were the first wholly–synthetic resins to be so developed, their chemistry is still not fully understood. The polymers derived from the interaction of phenols and formaldehyde differ in one important respect from other polycondensation products, in that polyfunctional phenols can commonly form a variety of isomerides of different chain length. Other products derived from polycondensation reactions, such as polyamides and polyesters are mixtures of molecular chains of various lengths, but for a molecule of a certain chain length only one structure is possible. As a result kinetic and related studies are feasible, on the assumption that the growth of a chain proceeds from one molecule to the next in a smooth and regular manner.

Polyfunctional phenols may react with formaldehyde in both ortho and para positions to the hydroxyl group giving numerous positional isomerides for any chain length. This peculiarity not only makes kinetic studies extremely difficult, but also makes the organic chemistry of the reaction very complex and tedious to unravel.

PF resins have been developed on purely empirical grounds. However, a better understanding of the chemical structure and mechanism of reaction of these resins that has been developed in the recent years has helped considerably in the production of high performance phenolic resins which have been designed for specific applications. Good knowledge of phenolic resin chemistry is thus an invaluable asset since it can provide for the design of high technology resins with specific physical properties.

1.1 CHEMISTRY

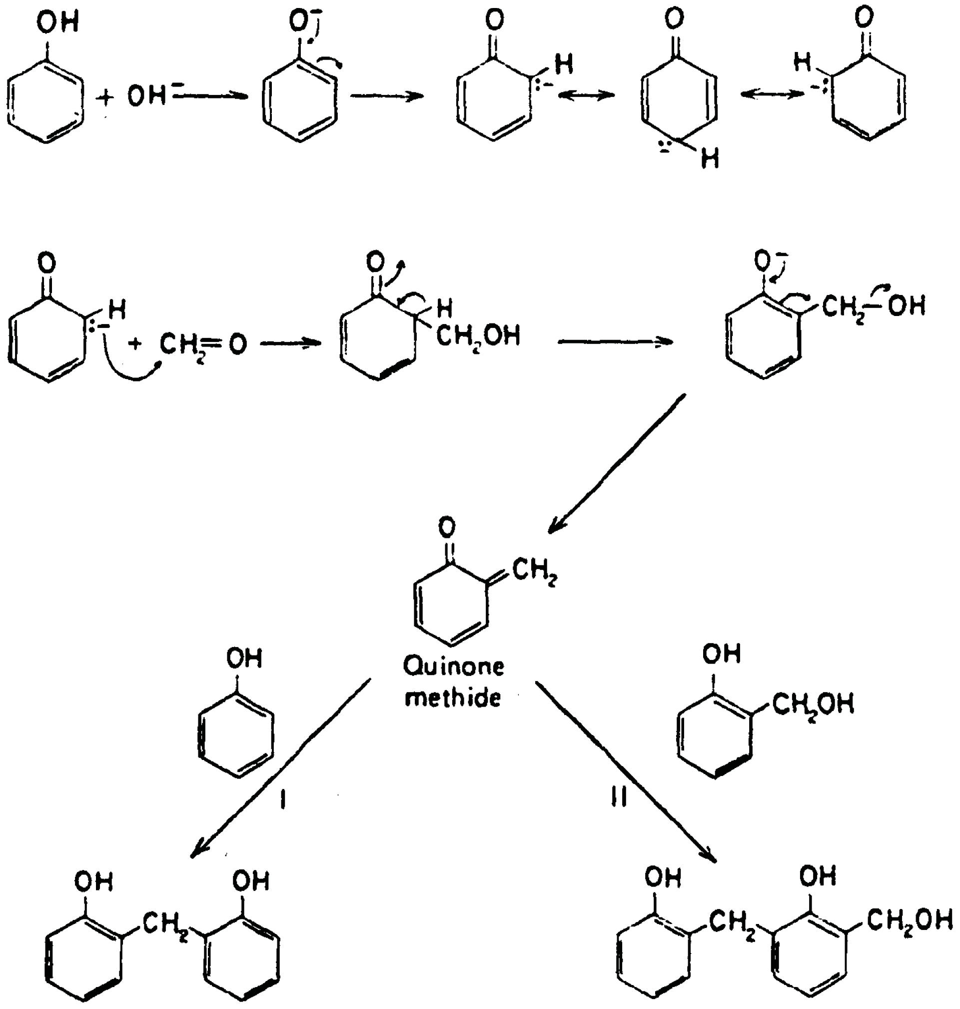
1.1.1 Reaction mechanisms

The type of catalyst and the molar ratio of the reactants used in the manufacture of phenolic resins largely determines the molecular structure and, therefore, the physical properties of the resins.

Methylolphenol or phenolic alcohol, and then dimethylolphenol are the products of the initial condensation of phenols with formaldehyde. The initial attack may be at the 2–, 4– or 6–position. The second stage of the reaction involves the reaction of the methylol groups with other available phenol or methylolphenol, leading first to the formation of linear polymers [1] and then to the formation of hard–cured, highly branched structures.

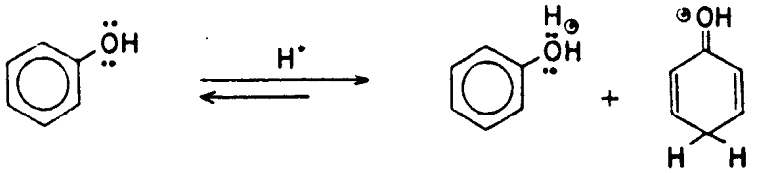
PF resins can be prepared by two different methods. The first involves the reaction of phenol with excess formaldehyde in the presence of an alkali catalyst. Mole ratios of formaldehyde to phenol of 1.8:1 – 2.2:1 are employed and the type of PF resin produced is usually referred to as "resol". The second production process for PF involves the reaction of phenol with a deficient amount of formaldehyde under acidic conditions; mole ratios of 0.8:1 – 1:1 are used to produce a hard resin known as "novolac".

Resols: a resol molecule contains reactive methylol groups. Heating causes the reactive resol molecules to condense to form large molecules, without the addition of a hardener. The function of phenols as nucleophiles is strengthened by the ionization of the phenol, without affecting the activity of the aldehyde.

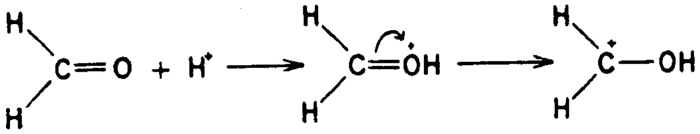


Phenolic nuclei can be linked not only be simple methylene bridges, but also by methylene ether bridges. The latter generally reverts to methylene bridges if heated during curing, with elimination of formaldehyde.

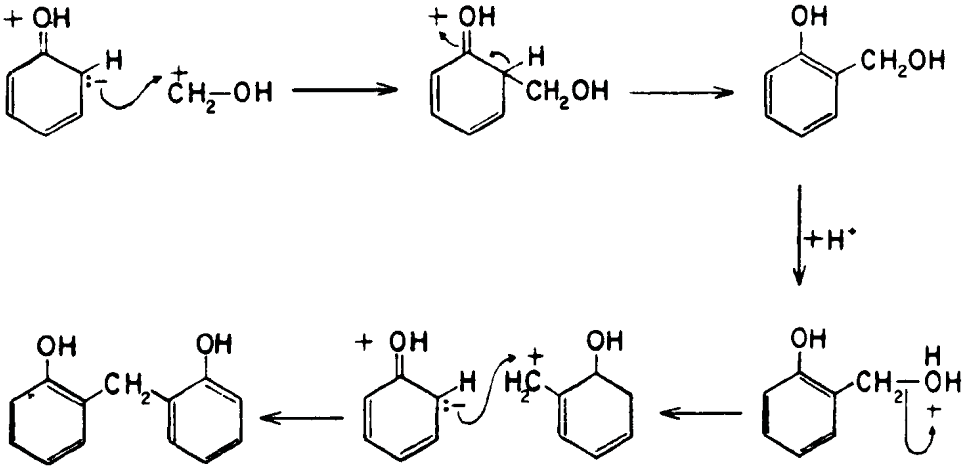
Novolaks: a novolak resin has no reactive methylol groups in its molecules, and therefore is incapable of condensing with other novolak molecules on heating without hardening agents. To complete resinification, further formaldehyde is required to cross link the novolak resin. Phenolic rings are considerably less active as nucleophiles at an acid pH, due to hydroxyl and ring protonation.



The aldehyde activation, however, which is brought by protonation compensates for the above reduction in potential reactivity. The protonated aldehyde is a more effective electrophile.



The substitution reaction proceeds slowly and condensation follows as a result of further protonation and the creation of a benzylcarbonium ion which acts as a nucleophile.



The difference between acid–catalyzed and base–catalyzed processes is (1) in the rate of aldehyde attack on the phenol, (2) in the subsequent condensation of the phenolic alcohols, and to some extent, (3) in the nature of the condensation reaction. With acid catalysis, phenolic alcohol formation is relatively slow and it is, therefore, the rate determining step of the total reaction. The condensation of phenolic alcohols and phenols forming compounds of the dihydroxydiphenylmethane type is instead rapid. The latter are therefore predominant intermediates in novolak resins.

In the base catalysis of the condensation of phenols and formaldehyde, the initial substitution reaction (i.e. the formaldehyde attack on the phenol) is faster than the subsequent condensation reaction. As a result, phenolic alcohols are the predominant intermediate species which then condense with either other methylol groups to form ether links, or more commonly, with the ortho or para positions in the phenolic ring to form methylene bridges. Water is eliminated in both cases

Unlike many thermoplastics, e.g. polyethylene, polystyrene, polysulfone, etc., phenolic resins are of relatively low molecular weight in the uncross–linked form. Novolaks are mixtures of isomeric polynuclear phenols of various chain lengths with an average of five to six phenolic nuclei per molecule. Mildly condensed liquid resols, which are the more important of the two types of phenolic resins in the formulation of wood adhesives, have an average of less than two phenolic nuclei in the molecule whereas the solid resols average three to four phenolic nuclei. In both alkaline and acidic conditions, the methylolphenols formed initially, condense with more phenols to form methylene–bridged polyphenols. The latter, however, quickly react in an alkaline system with more formaldehyde to produce methylol derivatives of the polyphenols. In addition to this method of growth in molecular size, methylol groups may interact with one another, liberating water and forming dimethylene–ether links. The average molecular weight of the resins obtained by acid condensation of phenol and formaldehyde decrease hyperbolically from over 1000 to 200, with increasing molar ratio of phenol to formaldehyde from 1.25:1 to 10:1 (Fig. 1.1).

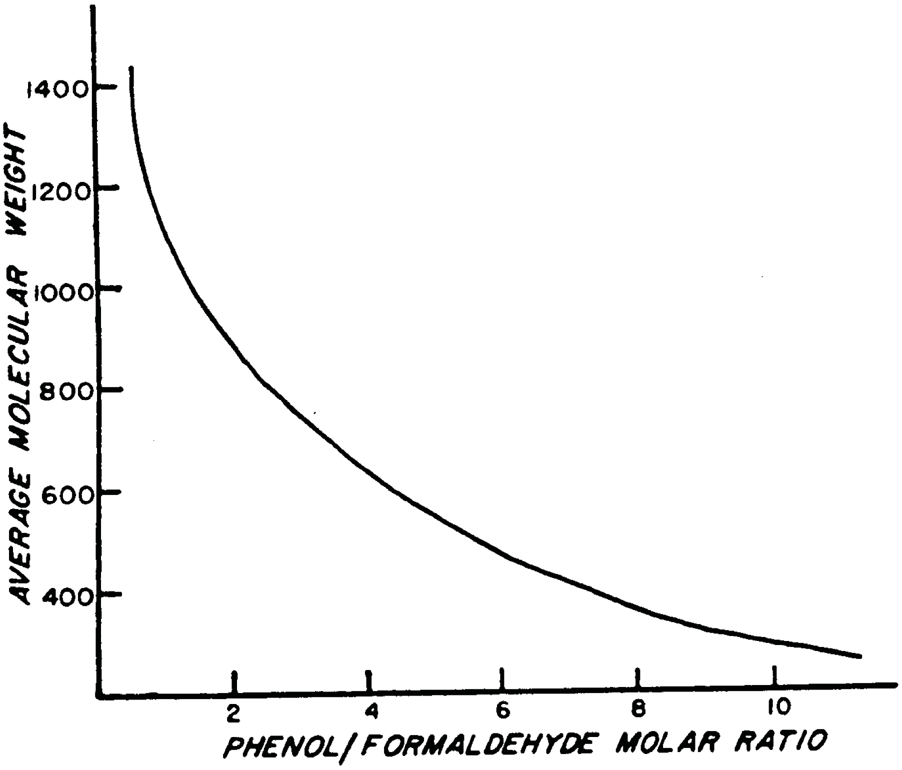
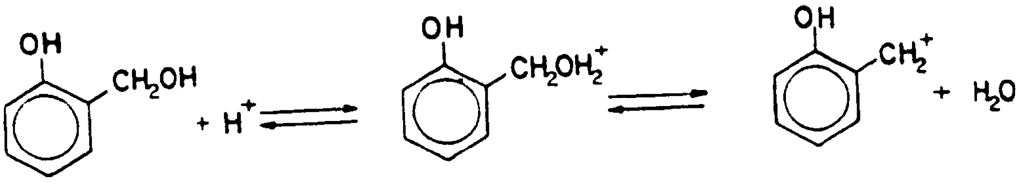


Fig.1.1 Average molecular weight of PF resins as a function of the phenol/formaldehyde molar ratio.

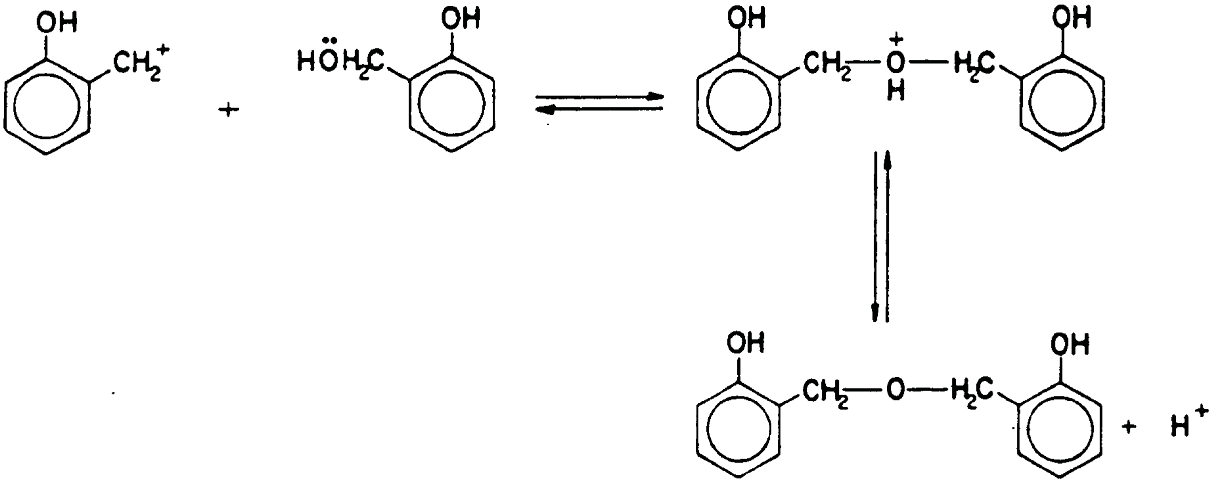
1.1.2 Mechanism: Methylene and Methylene–Ether Bridges

The mechanism of condensation of phenol with formaldehyde can be separated into two phases [2]. Condensation is almost definitely ionic in the presence of water in the early stages. At a later stage, when the reaction proceeds in unreacted phenol as the solvent, after dewatering, it is almost definitely non–ionic. The ionic mechanism was formulated [2] as follows:



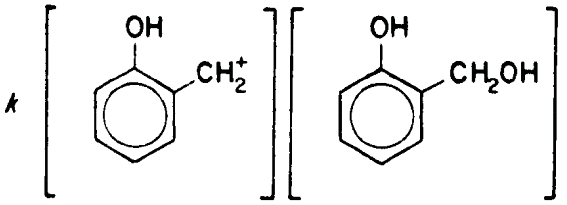
followed by the two reactions below:

1)

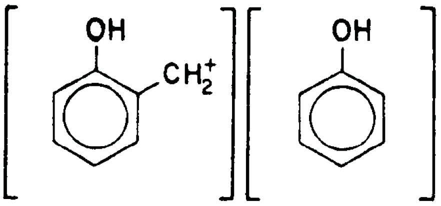


(2)

The rate of ether formation is

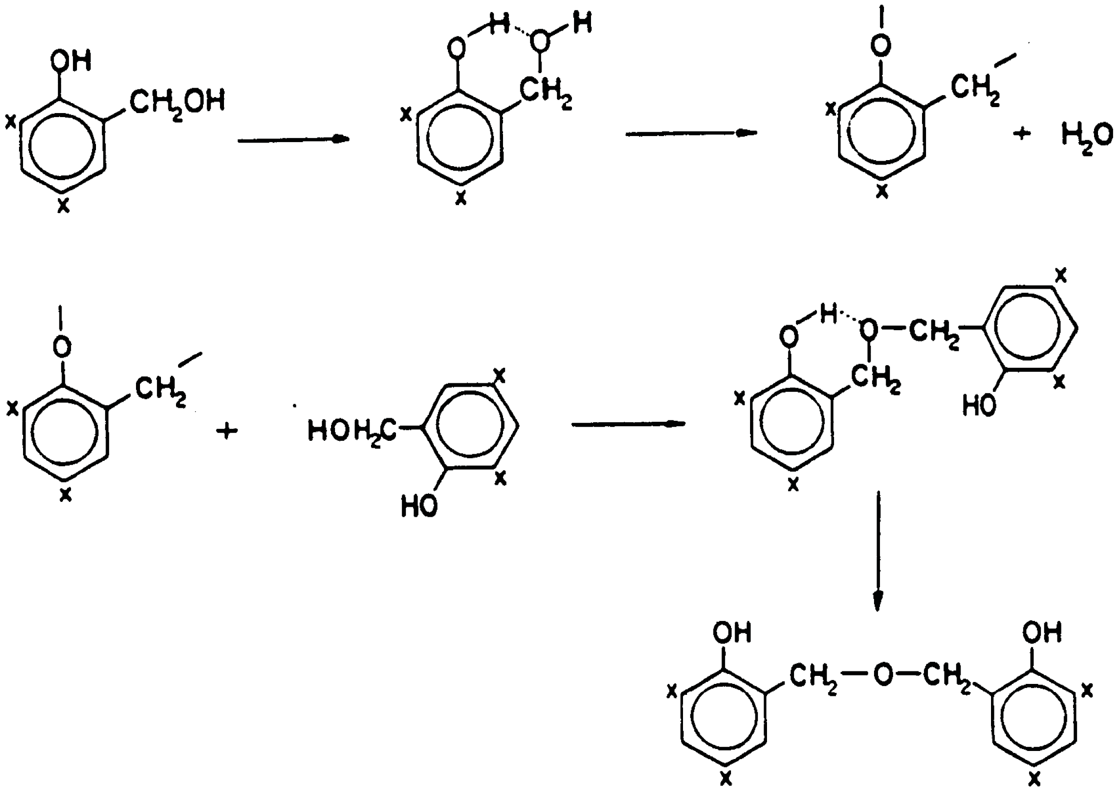


and the $-CH_2$ link



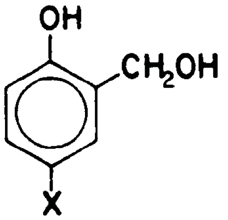
A methylene bridge is more likely to be formed than an ether link under acid conditions and when free positions in uncompletely reacted phenol are available. Ethers can be formed only within limited and critical pH ranges, and then only at slow rates.

In the later stages of phenolic resin formation and in the heat hardening of phenolic alcohols a non–ionic mechanism is more likely to occur. Since the reaction cannot involve a carbonium ion, it will probably use an intermediate of the quinone methide type. This compound is probably generated by a hydrogen–bonding mechanism. This has been shown to occur in phenol alcohols and dibenzyl ethers [2,3]. In the case of a monoalcohol, the reaction will be

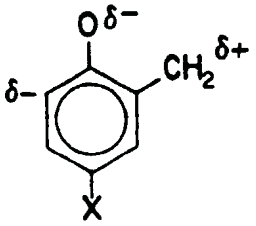


A quinone methide type radical is likely to have a considerably long life and yield a dibenzyl ether easily and a methylene bridge with difficulty. Ortho–methylolphenols produce ethers more readily than the para–alcohols.

This non–ionic mechanism explains both the known reactions of phenol monoalcohols and also covers fully substituted dialcohols. The case is different for partially substituted monoalcohols.



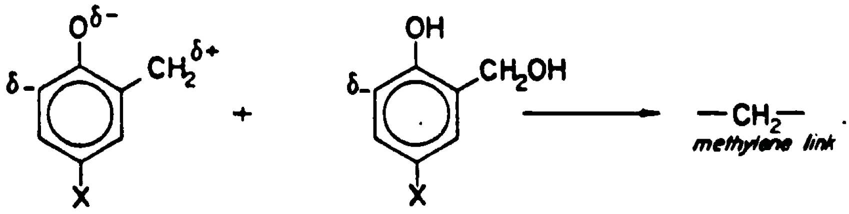
Partially substituted monoalcohol



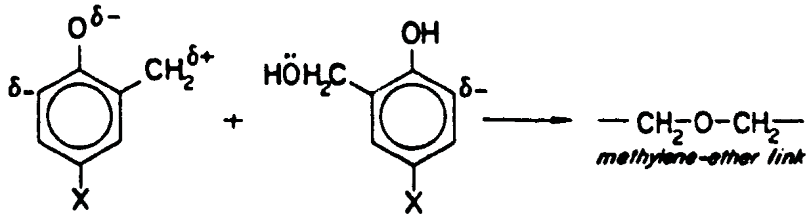
Intermediate

This intermediate has a definite choice of reactions:

(a)



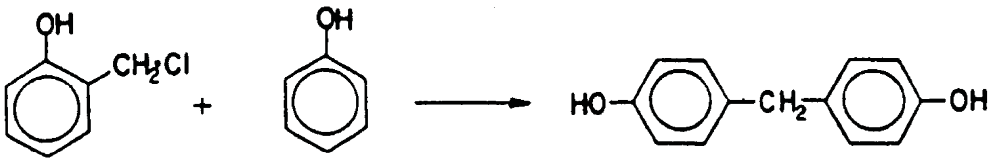
(b)



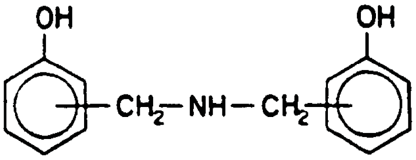
Reaction (a) is much more likely to occur and the formation of ethers is improbable. Experimental evidence supports this view. Thus, one can conclude that in the hardening of phenol alcohols which have free positions for substitution by methylol or its equivalents, a methylene bridge rather than an ether link will preferably be formed. Under ionic conditions, there is a limited range of pH values in which ether can be formed. However, this does not correspond with the working conditions of generally used pH.

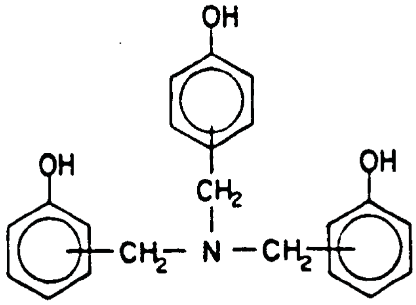
1.1.3 Catalysis in Phenol Formaldehyde Condensation

The catalyst employed in a phenol–formaldehyde reaction plays an important role since it can determine to a great extent the final structure of the resin. When, for example, hydrochloric acid is employed in an acid catalysis the reaction is highly selective and takes place in the para position.



As regards alkaline catalysis, different mechanisms can operate according to the alkali used. In the case where sodium hydroxide is used as the catalyst, the mechanism probably involves the formation of a chelate ring. When ammonia is used as a catalyst, the resins formed are very different in some of their characteristics from other alkali–catalyzed phenol formaldehyde resins. Intermediates containing nitrogen are formed. Similar types of intermediates are formed when amines or hexamethylenetetramine are used instead of ammonia. In the case of ammonia, the main intermediates are dihydroxybenzylamines and trihydroxylbenzylamines [4].

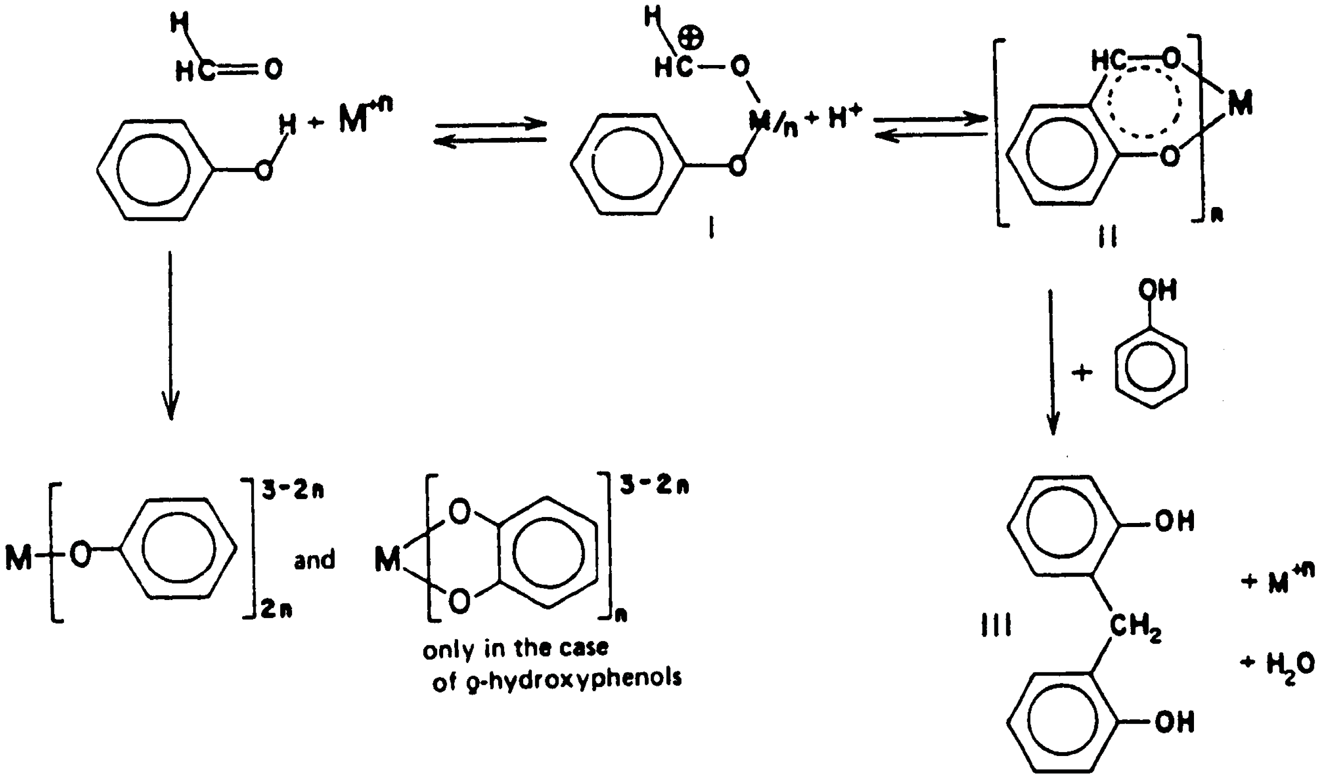




These intermediates react further with phenol, causing the splitting and elimination of the nitrogen thus producing nitrogen–free resins. This, however, requires a considerable excess of phenol and a high temperature. Increasing the phenol– hexamethylenetetramine ratio from 3:1 to 7:1 the nitrogen content on heating at 210°C is reduced from 7% to less than 1%.

The more ammonia–, amine–, or amide–catalyst is used in phenolic resin condensation, the higher the molecular weight and melting point which are obtained, without cross–linking. Ammonia, amines and amides (particularly dimethylformamide) are sometimes used as accelerators during the curing of phenolic adhesives for wood products.

Metallic ions catalysis is very important as it can alter the rate of curing of phenolic resins to a great extent. In phenolic resins prepared by metal ions catalysis there is a preferential ortho methylolation and therefore a high proportion of ortho–ortho links in the uncured phenolic resins. Normal condensation yields roughly equal quantities of para–para and ortho–para links, but uncured resins produced by metal ions catalysis yield approximately one ortho–para to two ortho–ortho links. Thus, the condensates formed have a higher proportion of free higher–reactive para positions available for further reaction during the curing of the resin. This is the reason why phenolic resins prepared by metal ions usually have higher rates of curing.



The metal ion can also have an inhibitory effect. It is the rate of metal exchange in solution and the instability of the complex formed that determine the accelerating or inhibiting effect of the metal in the reaction of phenol with formaldehyde. The more stable complex it is, the slower the reaction proceeds to the formation of resin III. The rate of reaction is directly proportional to the instability, or the rate of metal exchange in solution of complex II.

The metal catalyst does not change its valence, but interacts with molecules or ions containing electron donor groups, and accelerates reactions in the same way as hydrogen ions do [5]. The acid catalysts due to the metal ion differs only in degree from that of the hydrogen ion [5]. The effect of the metal, however, is stronger than that of hydrogen ions, because of higher charge and greater covalence. This is very important for the preparation of phenol–formaldehyde adhesives for wood where very low pH values cannot be used because they cause wood deterioration. This allows phenolic resin adhesives to set in milder acid conditions, without any wood deterioration or extension of the setting time. Most bivalent metallic ions act as accelerators in the phenol–formaldehyde reactions, whereas electropositive trivalent metallic ions generally inhibit or retard them. The extent of the metal ions accelerating effect is

$Pb^{III}, Zn^{II}, Cd^{II}, Ni^{II} > Mu^{II}, Mg^{II}, Cu^{II} > Mn^{III}, Fe^{III} >> Be^{II}, A\ell^{III} > Cr^{III}, Co^{II}$.

The most recent findings [6] show that a molar excess of phenol is not necessary for the effect to take place. This is in opposition of the original theory. It was also found [6] that the efficiency of the metal ions on a molar basis is fairly independent of the stability of the complexes formed, but is directly dependent on the rate of metal ion exchange in solution.

However, the most important conclusion is that the accelerating effect is present in both the manufacture of the phenol–formaldehyde resin and its curing. Therefore, the fast rate of curing on high–ortho phenolic resins can be only partially described to the high proportion of para positions available. The other reason for the fast rate of curing is that the metallic ion catalyst is still present and free to act, in the resin at the time of curing. Such a resin has a considerable number of ortho positions that are still available for reaction, and capable of complexing.

The initial formaldehyde attack is the rate determining step of acid–catalyzed phenolic reactions. The accelerating effect of the metal ions occurs throughout the whole pH range, but is particularly evident in the range 2.5 – 7. The anion also influences the effectiveness of the metal as an accelerator of the reaction. For example, the following scale represents the decreasing accelerating effect for Zn^{2+} anions:

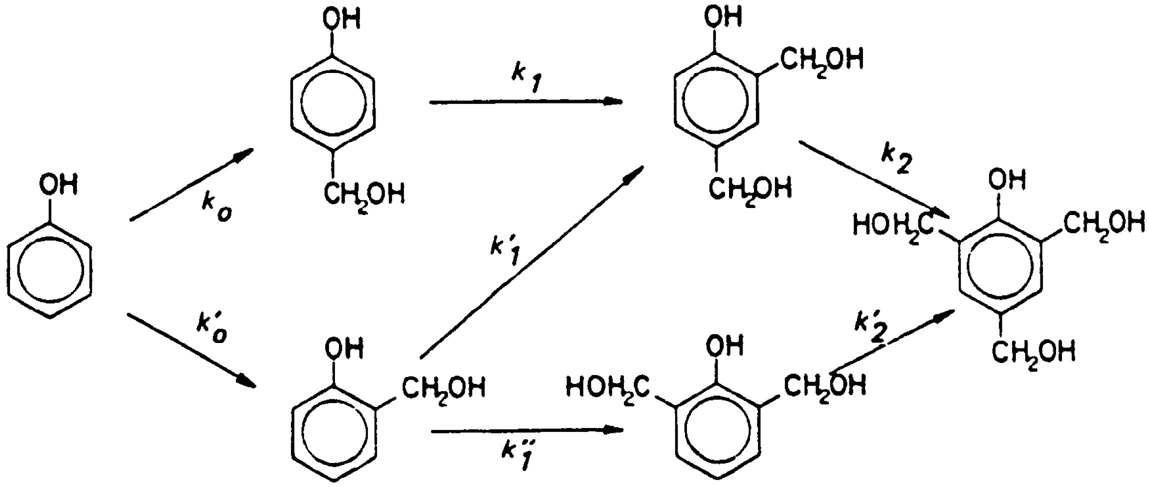
$$Zn(CH_3COO)_2 > ZnC\ell_2 + CH_3COONa > ZnC\ell_2$$

The anion effect can be explained in terms of the relative affinities of the metal for the anion used and the complex formed.

1.1.4 Reaction Kinetics

The reaction of phenols with formaldehyde has been investigated by many researchers. The most comprehensive and detailed investigation was done by Freeman and Lewis [7]. The following information comes from their investigation into the kinetics of the reaction of phenols with formaldehyde.

They reacted phenol, ortho–hydroxybenzyl alcohol (saligenin), para–hydroxybenzyl alcohol, or 2.4 – 2.6–dihydroxymethylphenol at 30°C with sufficient formaldehyde (as formalin) to bring about complete substitution, in the presence of 1 mole of sodium hydroxide per mole of the phenol. The reactions that occurred are summarized in the following diagram.



The following conclusions were drawn from this study:

1. The para position in phenol has a greater affinity for formaldehyde than the ortho position (i.e., 6.2 as compared with 5.25). Nevertheless, saligenin is produced 1.7 times more quickly than para–isomeride because there are two ortho positions available.

2. The reactivity of the nuclear positions towards formaldehyde is decreased by the introduction of a methylol group. Para–hydroxylbenzyl alcohol is 50% less reactive than phenol (i.e., 7.5 as compared with 16.7), even though it has two–thirds the number of positions still available.

3. The deactivation due to a methylol group into the ortho position is little. Therefore, saligenin is twice as reactive as para–hydroxylbenzyl alcohol, and almost as reactive as phenol. Similarly, 2.4–dihydroxymethylphenol is more reactive than para– hydroxybenzyl alcohol, and slightly more than half as reactive as saligenin.

Table 1.1 Reaction Rate Constants for Methylol Phenols + Formaldehyde

	Second–order rate constant $\times 10^{-6}$
Phenol– $\xrightarrow{k_0}$ *p*–monomethylol phenol Phenol– $\xrightarrow{k_0'}$ *o*–monomethylol phenol	$k_0 = 6.2$ $k_0' = 10.5$
p–Monomethylol phenol $\xrightarrow[k_1']{k_1}$ 2,4–dimethylol phenol	$k_1 = 7.5$ $k_1' = 7.3$
o–Monomethylol phenol $\xrightarrow{k_1''}$ 2,6–dimethylol phenol	$k_1'' = 8.7$
2,4–Dimethylol phenol $\xrightarrow[k_2']{k_2}$ 2,4,6–trimethylol phenol	$k_2 = 9.1$
2,6–Dimethylol phenol	$k_2' = 41.7$

Taking the reactivity of the ortho position of p–hydroxybenzyl alcohol as unity, the relative reactivities of the ortho and para positions of phenol are 1.4 and 1.7, respectively. Saligenin ortho and para positions have the relative reactivities of 2.3 and 2.0. The 2.4–dimethylolphenol ortho position has a value of 2.4. The 2.6–dimethylolphenol para position has a value of 11.1.

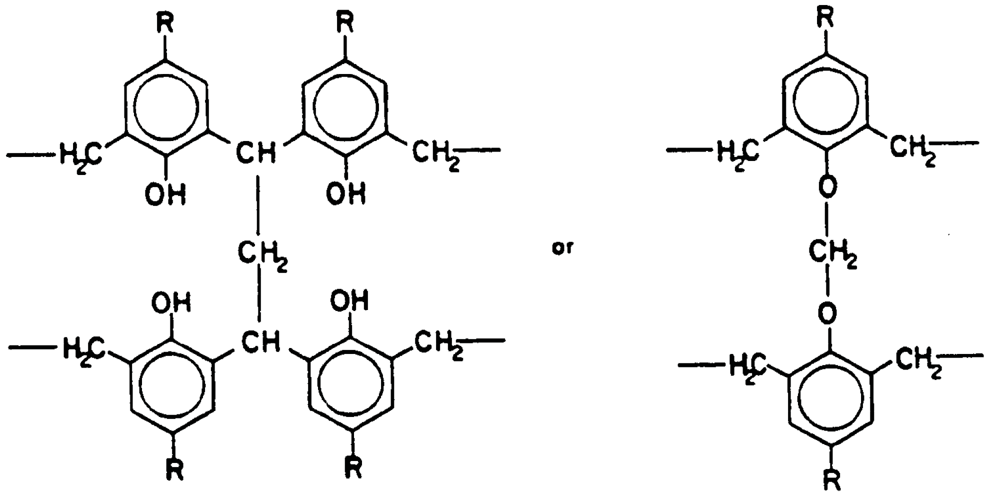
1.1.5 Cure of Phenolic Resins

When resols, or A–stage resins are heated to temperatures above 100°C, their viscosity increases and eventually they become rubbery. Then they belong to the resitol or B stage and they are insoluble in solvents like alcohol and water but they swell in acetone and flow under heat and pressure. With further heating the resins enter the resite or C stage. The are insoluble and infusible.

The above changes are due to structural changes that take place. The low molecular weight mono– and poly–alcohols, stage A, become partly linked polymers, stage B, and finally branched and cross–linked three–dimensional networks, stage C. Novolaks can also undergo these changes but methylene–supplying agents are required under alkaline conditions. Branched novolaks cure faster than linear novolaks. The same changes can be obtained by adding strong acids to low molecular weight liquid resols. Such condensation of the methylol groups with the phenolic nuclei may be exothermic enough to reach temperatures high enough to complete the hardening. With sufficient acid catalysis, thin films of resols can harden at room temperature.

The mechanism of hardening of phenol–formaldehyde resins takes place in two stages. In the first stage of hardening adjacent methylol groups condense forming ether–linked polymers with elimination of water.

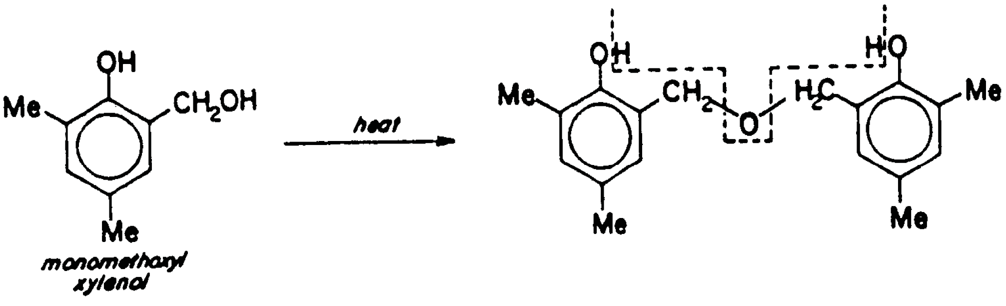
The secondary stage of hardening at higher temperatures is accompanied by a change of colour from pale yellow–red to dark brown. There are several theories as to what happens during the secondary breakdown of the primary ether–linked network. When the ether links revert into methylene bridges, one molecule of formaldehyde is released from each link. Since only half of this is obtained, it may be assumed that the released formaldehyde reacts with any remaining reactive positions on the phenolic nuclei, or with the methylene bridges or the phenolic hydroxyl groups. This gives rise to the following structures:



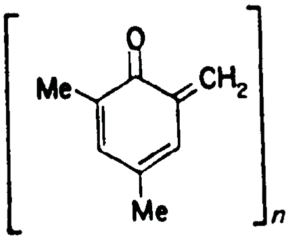
These reactions involve further water formation which is in fact observed.

Another theory disagrees with the above approach that liberated formaldehyde causes cross–linking by condensing with methylene bridges.

This is based on the finding that dihydroxydiphenylmethanes do not react with formaldehyde not even at 200 – 240°C. Also, monomethylolxylenols, which have no free reactive positions, resinify on heating with a loss of water and formaldehyde. The initial product obtained is an ether, namely



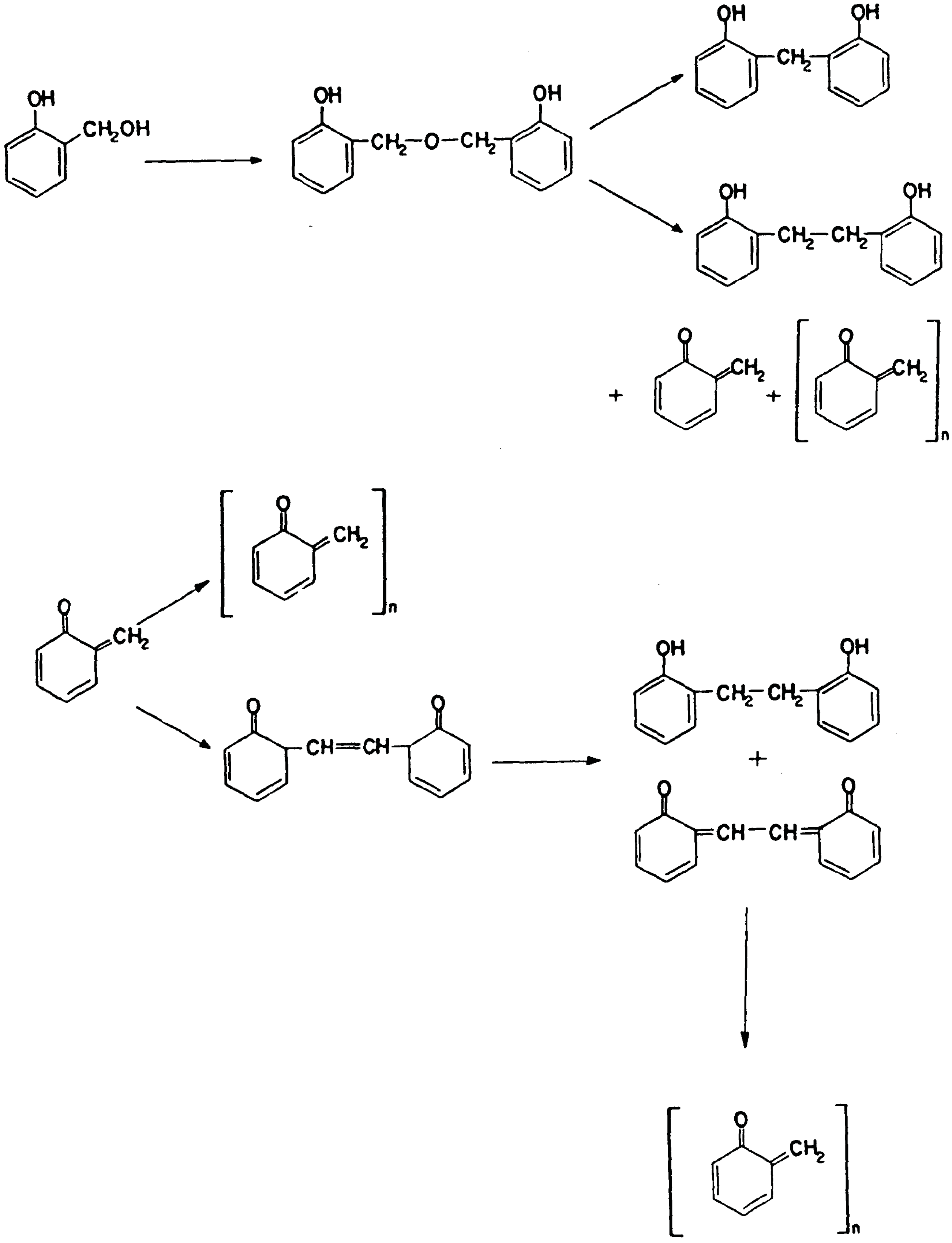
On further heating a considerable amount of polymeric quinone methide is obtained, formed by loss of water from the ether shown above and further polymerization.



polymeric quinone methide

The polymeric quinone methide, which has an average degree of polymerization of between 2 and 3, resinifies at 220°C and turns black without liberating water or formaldehyde. It is likely that hydrogenation and dehydrogenation at these reactions occur at fairly high temperatures, simultaneously converting the polymeric and monomeric quinone methides to diphenylethanes, aldehydes, alkyl phenols, and undistillable resins.

A schematic representation of the above theory is shown below:



Summarizing, during the process of hardening at 140°C, methylol and dimethylolphenols give products containing methylene bridges and methylene–ether links, with molecular weights of approximately 5000. The methylene links are stable whereas the ether links are stable only up to 160°C. At higher temperatures, quinone methides are readily formed. These polymerize into inert resins at 200 – 230°C. Hydroxyaldehydes are also formed through the quinone methides or by direct cracking of the ether chains.

Phenol–formaldehyde resols, harden in an alkaline environment because of the formation of mainly methylene links, very few quinone methides and no ether links. The fully hardened resins are rigid three–dimensional structures in which cross–linking is random. It is pressumed that at certain points throughout the mass relatively large holes occur which are points of weakness. This is a result of the structure and arrangement of the original molecules [8] and may be also a result of trapped water or catalyst molecules. As a result of these points of weakness, the tensile strength of the hardened resin is very much less than in theory.

1.2 PHYSICAL PROPERTIES OF PF RESINS

PF resins are typically brown in colour, and novolaks are lighter than resols. Resols are dark yellow, orange reddish, or brownish. However, if the alkali is neutralized, resols become almost colourless. Cured PF resins have a specific gravity of approximately 1.2 – 1.3, a refractive index of 1.6, and a specific heat of 0.5.

Generally, PF resins in the A stage are readily soluble in alcohol, esters, ketones, phenols, and some ethers, and insoluble in hydrocarbons and oils. Resols tend to be more soluble in alcohols and water, and novolaks tend to be more soluble in hydrocarbons. Especially resols that are derived from phenol, during the early stages of condensation tend to be water soluble because of the presence of methylolphenols, especially polyalcohols. Cresylic resols are less soluble, and xylenolic resols almost insoluble in water. The alcohol and water solubility can be reduced by using acetaldehyde or other aldehydes instead of formmaldehyde, and also by introducing hydrocarbon chains, particularly in the ortho or para position in the aromatic ring. B–stage resins are onle soluble in boiling phenols, and acetone, aqueous sodium hydroxide, and deca– and tetrahydronaphtalenes. Hardened or C–stage resins are relatively stable up to about 200°C. Hardened resins are also very resistant to most chemical reagents. They dissolve slowly in boiling phenols such as naphtols, whereas resins from the simplest phenols can also be broken down and dissolved by hot, strong, alkali solutions. Cresol–formaldehyde and especially xylenolformaldehyde resins, however, are much less susceptible to attack. The chemical resistance of the PF resins is strongly influenced by the filler compound used. Inert mineral fillers have a better resistance than cellulosic fillers. C–stage resins are resistant to most acids, except sulfuric acid stronger than 50%, formic acid, and oxidizing acids such as nitric and chromic acids. The amount of resin which is insoluble in acetone is proportional to the curing temperature. The higher the hardening temperature, the lower the amount of acetone extractives. The degree of cure of the resins is tested by the insolubility of hardened resins in acetone. The mechanical properties of hardened phenol–formaldehyde resins are greatly influenced by the moisture content. This applies even more to resins containing fillers, plasticizers, and other ingredients. It is, therefore necessary when measuring the mechanical properties of resins, to condition the test pieces under controlled temperature and humidity before making the tests. The type and orientation of fillers also affects the mechanical properties of the hardened resins.

The array of physical properties that arise from the synthetic options has made possible an extremely large number of applications for the phenolic resins. These applications include

(1) moulding powders (i.e. "Bakelite")
(2) walls bonding undercoats (painting)
(4) foundry core resins
(5) industrial wood adhesives (i.e. particleboard, plywood)
(6) high–technology extrudable thermosettings
(7) modifiers to impart high temperature resistance to other resins (i.e. epoxies)
(8) brake pads
(9) fire and water resistant rigid foams, etc.

The worldwide usage of phenolic resins is approximately 1.5 – 2.0 million tons per annum.

1.3 PHENOLIC RESIN ADHESIVES FOR WOOD

Phenolic resins for wood products are mainly resol–type. Novolaks are of less interest in this application. The novolaks used in the wood industry are phenol–formaldehyde resols that have been transformed into novolaks by blocking the methylol groups present with resorcinol, or resorcinol–formaldehyde novolaks.

The point of lowest reactivity for all phenolic resins is a pH of about 4. The effect of the pH, and the phenol/formaldehyde molar ratio on the rate of polymerization of phenolic resols is shown in Figure 1.2.

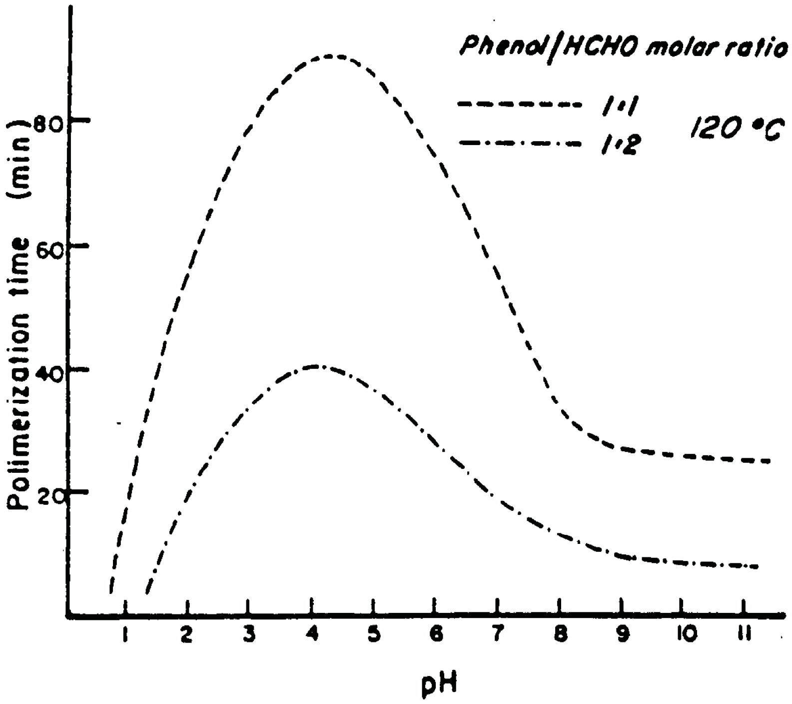


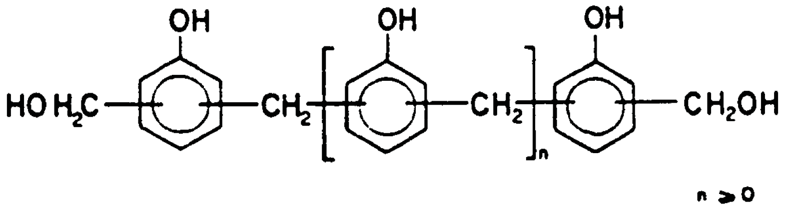
Fig. 1.2 Rate of polymerization as a function of pH for phenolic resols of different molar ratios at 120°C.

1.3.1 Plywood and Particleboard Adhesives and their Application

Because of their superior water resistance, phenolic resins are preferred as binders for exterior–grade plywood and particleboard.

In the manufacture of particleboard, the adhesives are sprayed onto the wood chips, or sprayed and spread by continuous blenders. The glued chips are formed in a mat and then pressed for 4 – 7 min., depending on the thickness and the moisture content, at 170 – 195°C and 25 – 35 Kg/cm². In the manufacture of plywood the adhesive is usually applied to the wood veneers by roller or extrusion coating and the veneer is then stacked and cured in a multidaylight press for 5 – 10 min. at 120 – 130°C, and at 12 – 16 Kg/cm².

From the phenolic resins only the resols are commercially used, for the production of plywood and particleboard. These resins have the following structure:



They cure by heating. In the case of particleboard, small amounts of wax emulsion and insecticide are added prior to curing. Vegetable or mineral fillers and tackifiers are added in the case of plywood. Accelerators are often added in both types of glue mixes. These are aminic or amidic (e.g. dimethylformamide) in the case of particleboard, and metallic salt catalysts (e.g., zinc acetate) in the case of plywood. The pH of these resins varies between 10 and 13.5, and is generally between 12 to 12.5.

Adhesion is at least 95% chemical in nature. The mechanical aspects of bond formation, such as keying cured adhesive solids into the wood surface, contribute negligibly to the bond strength or wood failure. The main chemical forces in thermosetting resin adhesion are primary valence bonds, covalent bonds, and hydrogen bonds, plus secondary forces such as van der Waals' and London's forces, and any other type of electrostatic, dipolar, and associative forces.

It is therefore essential that the resin contains significant numbers of functional groups and that the wood surface has a significant number of reactive sites to enable the resin to bond. Thus, adhesion is inhibited by any factors that limit resin functionality or block reactive sites on the wood. Some of the factors that affect adhesion are discussed below (see 1.3.5, 1.4.1, 1.4.2).

1.3.2 Phenol–Formaldehyde Structures in Relation to their Adhesion to Wood Cellulose [9]

In a study on the phenol–formaldehyde structures in relation to their adhesion to wood cellulose [9], Pizzi and Smit suggest that in the case of interaction of PF resins with cellulose, adhesion resides mostly with the attraction between resin and adherend due to secondary forces between noncovalently bonded pairs of atoms and atom groups. Although formaldehyde and formaldehyde–based resins do react covalently with cellulose forming other linkages and cross linking the cellulose fibres, these reactions only occur to a limited extent. Also, the contribution of such covalent bonds to the PF adhesion in the bonding of lignocellulosic materials does not appear to have been assessed either qualitatively or quantitatively. Thus, the covalent bonding contribution was disregarded in this study. Pizzi and Smit used a conformational analysis approach in order to obtain a better understanding of the phenomenon of adhesion by means of calculations of all the values of the secondary interactions between the noncovalently bonded atoms of the two molecules involved (i.e. P–F oligomer and crystalline cellulose I). In this theoretical study it was shown that there is a stronger affinity between PF and cellulose than between water and cellulose. This implies that the resistance to weather and water of PF–lignocellulosic materials is due to both the imperviousness of the cured PF resin and the imperviousness of the adhesive/adherent interfacial bond. Consequently, this implies that in adhesives where the adhesive/adherend interfacial bond is not impervious to water attack, and/or where the water resistance of the resin itself does not protect the interfacial bond, lower water resistance joints may result.

The fact that cellulose constitutes as much as 50% of wood, this study implies applicability to a wood substrate. The finding that configuration of the adhesive molecule has a marked influence on the energy of adsorption, and hence on adhesion, is interesting since the use of conformational analysis can indicate how the preparation of an adhesive should be changed to obtain optimum adhesion.

1.3.3 The Correlation Between Preparation and Properties in Phenolic Resins [10]

Wood is a dimensionally anisotropic, chemically heterogeneous substrate, and its properties are strongly influenced by climatic conditions such as temperature and humidity. The composite's properties are influenced by wood particle size and geometry, and by manufacturing process variables. An effective adhesive bond and useful wood/adhesive composite is based on the ability of the resin chemist to manipulate the chemistry of the resin system to fit the properties of the wood and the bonding process to allow for the desired "marriage" of wood and adhesive. As new or modified composite processes appear in the marketplace, additional demands are placed on the resins used in these products. Thus, resin chemists have evolved into polymer engineers, using current resin characterization techniques in conjunction with an interdisciplinary approach to problem solving.

The identification of variables that correlate to resin performance is the prime objective of resin and characterization studies. Some of the most important variables and their interactions are shown in Figure 1.3.

Product performance optimization of a given manufacturing process generally results in a unique resin for that application. It is not possible to formulate a "universal resin" for all applications. Some trends of structure/property data found in literature are listed in Table 1.2.

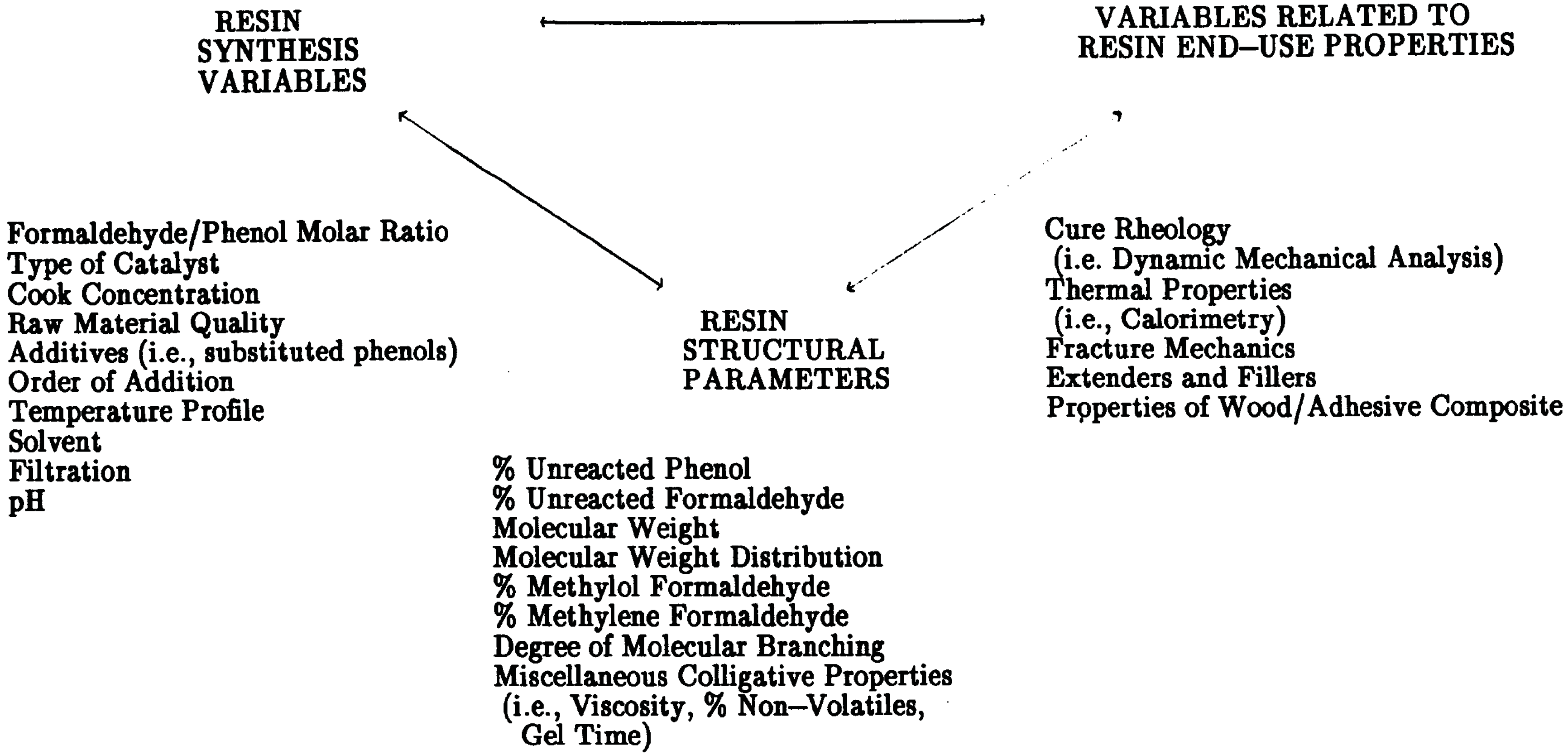


Fig. 1.3 Interaction of resin synthesis, structure and property relationships

Table 1.2 Some Structure/Property Relationships Documented in the Literature

Resin synthesis or structural variable, or process variable		Ref.
PF's varying in F/P and NaOH/P studied by TBA	1. Initial rigidity and damping are strongly influenced by resin MW and viscosity. 2. Cured rigidity is influenced by F/P and total NaOH/P molar ratio, reaching a maximum at F/P = 2.5 and total NaOH/P = 0.75, the highest levels studied. 3. Highly branched resins were more rigid.	11
PF resins differing in MW, degree of branching, oligomer content, and process assembly time.	1. MW was inversely related to bond quality at long assembly times. 2. High free phenol and orthomethylol phenol helped plasticize high MW resins. 3. Highly branched resins flow poorly at long assembly times. 4. Extenders mask intrinsic resin properties. 5. Thicker glue lines perform better.	12
Cured PF resin differing in F/P, NaOH/P studied by TBA and fracture mechanics	1. Fracture toughness is inversely related to cured resin rigidity. 2. Cured resin rigidity is inversely related to NaOH/P cook molar ratio between 0.15 and 0.35, and directly related to F/P molar ratio between 2.2 and 2.5. 3. Extended resins have higher fracture toughness than neat resins.	13

Table 1.2 continued

PF, PRF, UMF, and PVA resin systems	1. Major rigidity changes during cure were characterized using TBA. 2. TBA is a dynamic measurement that allows separation of elastic (rigidity) and viscous (damping) components of resin cure.	14
Wood–epoxy resin bond systems	1. Thinner glue lines had higher stress concentration. 2. More rigid glue lines had higher stress concentration. 3. Cleavage fracture toughness could be improved by increasing flexibility of the cured resin or by increasing glue–line thickness.	15
F/P ratio and NaOH/P ratio	1. Bond strength was generally poorer in resins with greater cure shrinkage. 2. Cure shrinkage was generally greater in resins with higher molar ratios of NaOH to phenol.	16
RF resin at low and high molecular weight, and low and high wood moisture content	1. Bond strength increased with increasing molecular weight at low moisture content and decreased with increasing molecular weight at the high moisture content. 2. Free vibrational and rate of strength development tests are useful for in situ observations of curing properties.	17

1.3.4 Characteristics of Plywood Phenolic Adhesives [18]

The phenol–formaldehyde plywood resins with the best performance have several properties in common:

1. Their alkali content is between one–third and one–half molar.
2. Phenolic resins for hardwood have lower molecular weight than the ones designed for softwood gluing.
3. They are high in methylol group content.
4. Phenolic resins for hardwoods, even in dried films or powdered resins, can be reliquified under heat and pressure to allow transfer and flow on the glue lines of a plywood panel.
5. Phenolic resins for hardwoods have higher thermal softening points than many other resins. This is an indication of more cross–links and greater durability after final cure.
6. They have a 40 – 45% solids content and 150 – 160 cp of viscocity at 25°C.

In general, softwood plywood adhesive resins are both more alkaline and more condensed. Exterior–grade plywood can be obtained from softwood by using these resins. Hardwood phenolic resins require about 30% longer press times. Phenolic resins for hardwood do not prepress as well as softwood phenolic resins. Prepressing is important as it minimizes face veneer losses and reduces precure times on hot platens. To increase the prepress capacity of low–alkali, long–flow phenolic resins suitable for hardwood, small amounts of starch or polyvinyl alcohol can be added to the resin glue mix just before use. Water–soluble thickeners (such as hydroxyethyl cellulose, polyethylene glycols, and maleic anhydride copolymers) contribute to prepress tack.