

CHAPTER 3



THEORY OF PHENOL-FORMALDEHYDE REACTION

The reaction between phenol and formaldehyde can be considered into three steps. 1) The addition of formaldehyde to phenol. 2) Chain growth or prepolymer formation. 3) The crosslinking or curing reaction. As mentioned in chapter 2, there are two prepolymer types which are obtained on different conditions. Novolaks are prepared in a strongly acidic pH region and at a molar ratio of 1 mole phenol to less than one mole formaldehyde. Resoles are prepared in an alkaline condition and at a molar ratio of 1 mole phenol to more than one mole formaldehyde. These two different conditions affect the difference in reaction kinetics and reaction mechanisms.

So this chapter proceeds with the reaction kinetic and mechanisms of phenol-formaldehyde reaction under acid and alkaline conditions and also the curing reaction of novolaks and resols.

Functionality of Phenols and Formaldehyde

The reactions of phenol and formaldehyde are based on the facts that formaldehyde has a functionality of two and that phenol has a functionality of three, because the hydrogen atoms in the two ortho and one para positions with respect to the phenolic hydroxyl group are quite reactive, while the hydrogen atoms in the two meta positions are considered as non-reactive. Thus, phenol and formaldehyde can react at reactive positions to yield a three-dimensional structure.

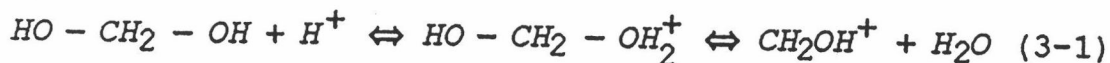
Reaction Under Acidic Conditions

The result of an acid-catalyzed reaction of less than one mole of aldehyde per mole of phenol is a novolak resin, which represents the result of a completed reaction and has no ability to continue growing in molecular weight. So curing must be accomplished by the subsequent addition of a crosslinking agent.

1. Reaction Mechanism

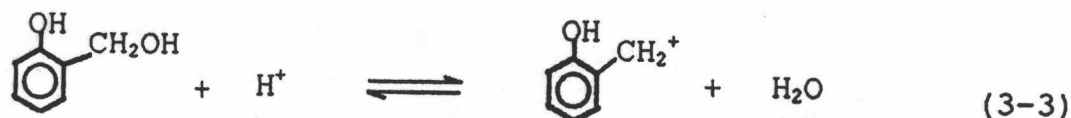
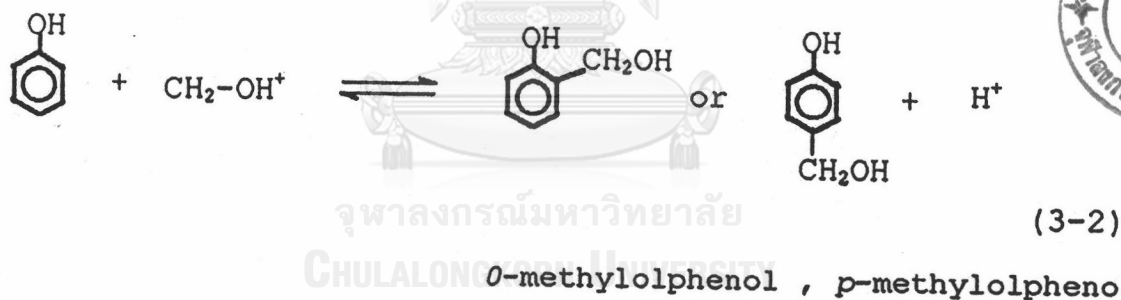
The general mechanism of the acid reaction concerns with an electrophilic substitution. In the first step, methylene glycol, which is the form of formaldehyde

in aqueous solution, is converted to the corresponding hydrated carbonium ion according to Eq.(3-1).



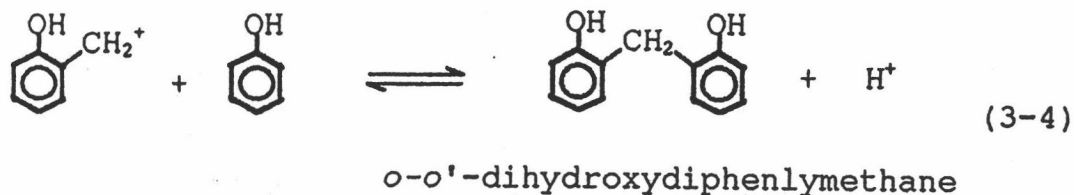
methylene glycol

The next step is the addition of the hydrate carbonium ion to the ortho and para positions of phenol with the elimination of water to produce *o*- or *p*-methylolphenol (Eq.3-2). Because the methylol group is an intermediate under acidic conditions, thus the benzylic carbonium ions are the results under these conditions according to Eq.(3-3).

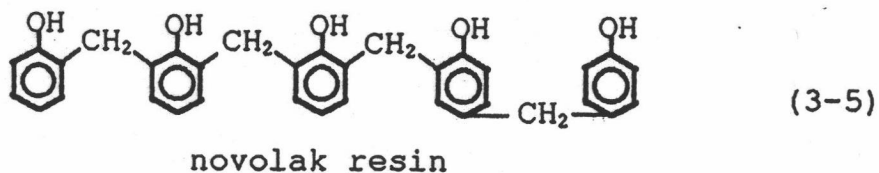


In the next step the benzylic carbonium ions react with free ortho and para positions on phenols to form dihydroxydiphenylmethane (Eq.3-4). There are three

isomer types of dihydroxydiphenylmethane: *o-o'*, *o-p'* and *p-p'* methylene linkage types.



Then these three isomers react with formaldehyde to form methylol derivatives which in turn react with more phenol to give polynuclear phenols connected by methylene linkage. These can be called novolak resins. Novolaks consists of a chain which usually contains five or six phenolic residues. Since an insufficient amount of formaldehyde is employed (at usual PF molar ratios of 1:0.70-0.85) in conjunction with acid catalysts, the formation of $-\text{CH}_2\text{OH}$ group or cross-linkages is limited. Thus cross-linking usually does not occur to any appreciable extent in novolak resins. Some studies proposed that branching occurred in novolaks which contained above 10 phenol units (Kamide, 1978 and Sojka, 1979). Computer simulation studies reveal that 2 branches are predicted for 10 units and 3 branches for 15 units (Ishida, 1981)



2 Reaction Kinetics

Analysis of the kinetics of the acid-catalyzed reaction is complicated by the fact that after the initial addition (substitution) of formaldehyde to phenol the resultant hydroxymethyl phenol condenses rapidly with phenol or phenol-end polymer molecules that may be present. The rate of formation of diphenylmethane (condensation reaction) was found to be more than five times (Martin, 1956) and 10-13 times (Malhotra, 1976) as fast as the formation of hydroxymethylolphenol.

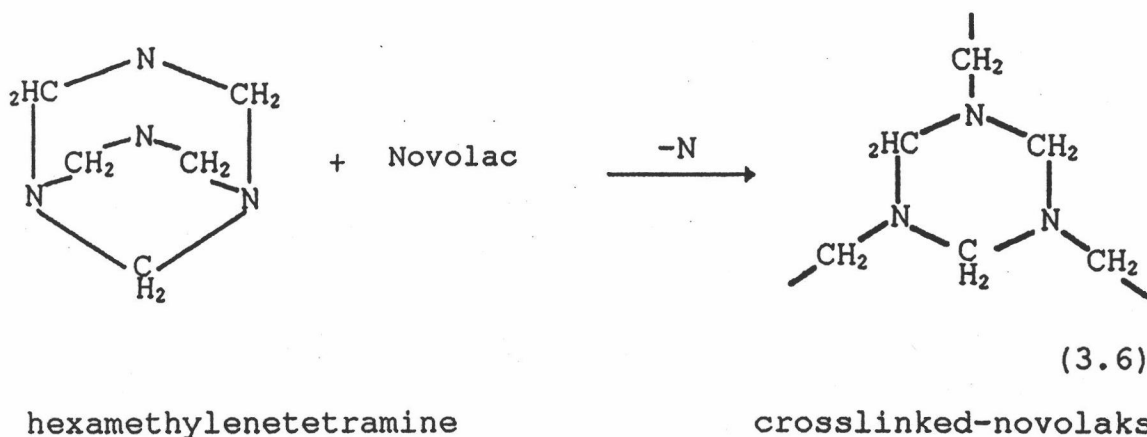
From the early studies, by starting with phenol alcohols and phenol, shown that the condensation is second order at any given pH (Kakiuchi and Otsu, 1952). The rate of the overall reaction to form polyhydroxyphenyl methane is a function of the acidity: the lower the pH is, the faster the reaction occurs. The data for only the addition reaction, which is the rate-controlling step, have not been developed. Study of the early stages of the over-all reaction at low pH (below 1.3) and low temperatures (30 °C) suggests a first-order addition (Jones, 1946). As the reaction proceeds and at pH above 1.3 and temperatures of 80-100 °C, the order of reaction seems to change to second order and to an order higher than second (Yanagita, 1942). The heat of the reaction measured by Jones was about 20 kcal/mole, which was close to his calculated values of 4.1 kcal/mole of

heat of addition plus 16.9 kcal/mole heat of condensation.

3. Curing of Novolaks

Curing or hardening of phenolic resins is a process which the resin is brought to a high enough degree of polymerization to be practical commercial value.

Curing of novolak resins requires the addition of a crosslinking compound, i.e., hexamethylenetetramine (hexa), trioxane, and paraformaldehyde. Hexa is the most widely used curing agent and is employed at 8-15 wt%. The usual reaction takes place in the presence of the linear methylene-bridged novolak molecules containing residual reactive ring positions, a small amount (about 5%) of free phenol, and often traces of moisture of the order of less than 1 %. Hexa has a tetrahedral structure and loss of any one of its nitrogen atoms leads to a structure with three active positions which can react with open positions on the phenolic rings of a novolak chain according to Eq.3.6. This releases ammonia, but no water occurs from the reaction. Any moisture liberated during cure would be a result of free water left in the original resin.



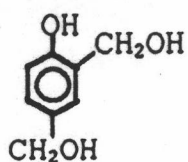
Reaction Under Alkaline Condition

The products of an alkaline-catalyzed reaction of more than one mole of formaldehyde per mole of phenol are resole resins, which are heat reactive. The products under alkaline conditions are isomers of methylolphenols according to Eq. (3-7)-(3-9)

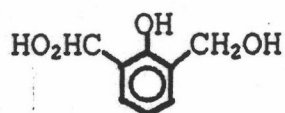


o-methylolphenol
(*o*-hydroxymethylphenol)

p-methylolphenol
(*p*-hydroxymethylphenol)

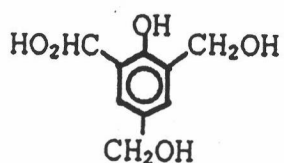


o,p'-methylolphenol
(*o,p'*-hydroxymethylphenol)



o,o'-methylolphenol
(*o,o'*-hydroxymethylphenol)

(3-8)

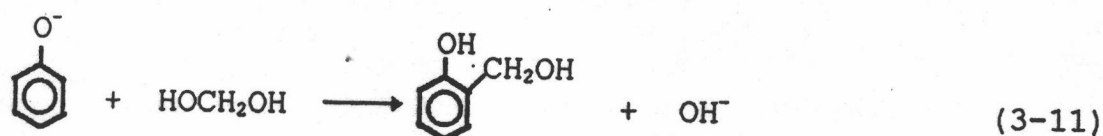
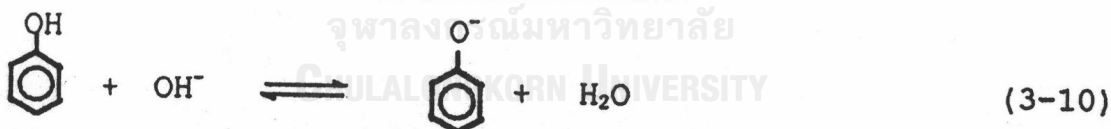


(3-9)

o,o,p-methylolphenol
(trihydroxymethylphenol)

1. Reaction Mechanism

In the first step, phenol reacts with alkaline to form the phenolate ion or phenolic anion according to Eq.3-10. The second step, the phenolate ion reacts with formaldehyde to form mono-, di-, and tri-methylolphenol according to Eq. 3-11. The reaction network of resole formation is shown in Figure 3-1 (Walker, 1964).



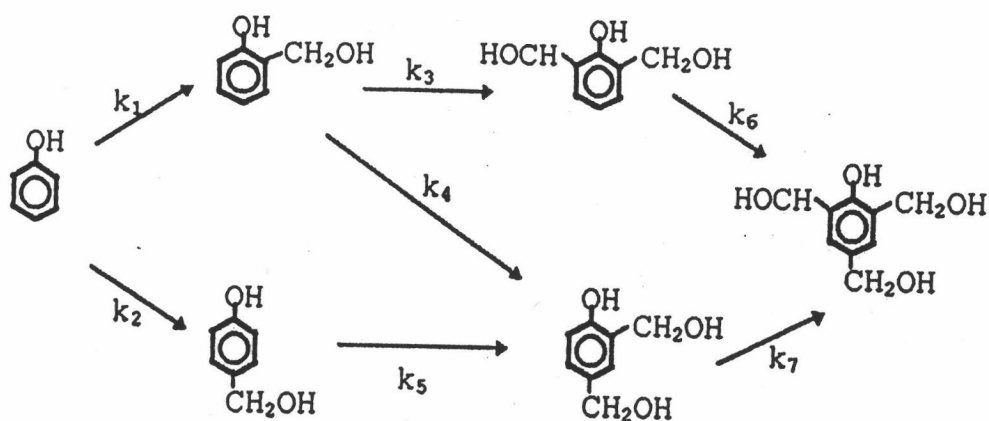


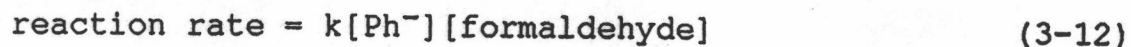
Figure 3-1 Reaction network of resole formation

2. Reaction Kinetics

The aim of any kinetic study is to determine how a reaction proceeds. However, the determination of reliable kinetic data for phenolic resin formation is complicated because the reaction conditions, including temperature, type and amount of catalyst, and mole ratios of reactants exert a profound influence on the results obtained. The identification of the reaction products is also relatively difficult. Therefore, it is not surprising that the reported kinetic data differ considerably. For the interpretation of kinetic data, it must be remembered that there are two *ortho*-positions in phenol and *o*-hydroxymethylphenol. Thus, the comparison of the relative reaction rates is more reasonable for the above mentioned reason.

The reaction catalyzed by ammonia (pH7,0-7.3) was found to be kinetically of the first order by Tsuruta (Tsuruta, 1936). The direct attack by measurement of the rate of consumption of formaldehyde was begun by Nordlander who also worked with ammonia-catalyzed systems (Nordlander, 1936). He found that the reaction was the first order and this has been confirmed by later workers (Sprung, 1941).

The order of reaction for systems catalyzed by stronger alkalines such as sodium hydroxide has been studied. Such systems are now recognized as second-order reactions which are dependent on the concentration of monomeric formaldehyde and phenolate anion according to Eq.3-12. These works are studied on the polymetylation of phenol according to the reaction scheme shown in Fig.3-1. Seven different rate constants are determined and reported as the relative reaction rates shown in Table 3-1 (Freeman and Lewis, 1954; Zsavitsas and Beaulieu, 1967; Eapen and Yeddana-palli, 1968).



According to Table 3.2, the para position at the start of the reaction towards formaldehyde is only slightly more reactive than either of the two ortho positions. However, o-methylolphenol is produced at a higher rate due to the fact that two o-positions are available. The ortho/para ratio was found to be 1.7. The

introduction of a para methylol group reduces the overall reactivity of the molecule, but the introduction of an ortho methylol group has an opposite effect. The conclusion of these reactions are as following: Firstly, *o*-methylolphenol are formed greater than *p*-methylolphenol, secondly, these mono-methylolphenols react with formaldehyde faster than phenol and thirdly, dimethylolphenols react with formaldehyde 2-4 times faster than phenol. As a result unreacted phenol remains high in resole resins even though the formaldehyde phenol ratio is as high as 3:1.

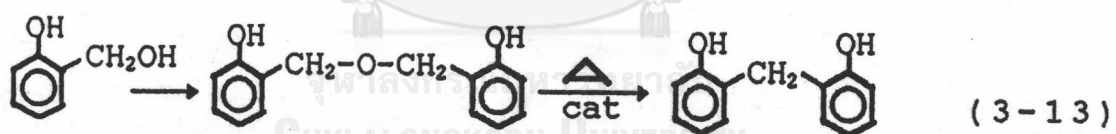
Table 3-1 Relative Rate Constants for Methylation of Phenol

Relative rate constant	Freeman and Lewis, 1954	Zsavitsas and Beaulieu, 1967	Eapen and Yeddana-palli 1968
k ₁	1.00	1.00	1.00
k ₂	1.18	1.09	1.46
k ₃	0.71	0.79	0.85
k ₄	1.39	1.80	3.00
k ₅	1.66	1.98	1.75
k ₆	7.94	3.33	4.36
k ₇	1.73	1.67	2.04

3. Curing of Resoles

Under curing of resole resin, no other ingredient (curing agent) is needed; the resin cures simply on the application of heat at temperature between 130-120 °C.

The pH and temperature influence the path and microstructure of the cured product. For example, using the model compound *o*-hydroxybenzyl alcohol, conversion to methylene ethers is high yield in the absence of a catalyst and at temperature under 130 °C according to Eq.3-18 (Sprung, 1949). With and acidic or basic catalyst and/or temperatures of 160 °C or higher, these methylene ether structures are mostly break down to methylene linkages with liberation of formaldehyde or water, or both.



Resoles are accounted for the largest percentage of phenolic resin product (Brode, 1982), since they have many industrial uses since they can be crosslinked to give thermoset plastics with desirable properties. Thus in this study, the alkaline catalyzed reactions are selected to be studied.