

Chapter 1

Introduction

1.1 Background and Preparation of Phenolic Resins

Phenolic resins are widely used condensation polymers. The polymers are useful because of their chemical resistance, electrical insulation, and dimensional ability. Their applications include the use in molding materials, industrial and decorative laminates, rubber modification, and in adhesives for making plywood, and bonding metals.¹ Phenolic resins are made from the condensation reaction of phenol and formaldehyde, which gives them another name, phenol-formaldehyde resins. These resins were first introduced by Pira in 1843.² However, these resins were not obtained as a commercial product until the work of Baekeland in 1909.³

Since phenolic resins have a wide range of applications, many research has paid attention to the effect of preparation conditions on the resin's properties. In fact, the variation of the phenol to formaldehyde ratio and the catalyst used in the preparation process are major conditions that affect the resin's properties. The first type of phenolic resin, resol, is synthesized from phenol and formaldehyde using an alkaline catalyst. The alkaline catalysts are usually NaOH, Na₂CO₃, KOH, K₂CO₃, Ba(OH)₂, NH₃, and RNH₂. The synthesis pathway of resol is shown in figure 1.1. Resol contain some reactive methylol groups in their molecules, which make them, upon heating, condense together to form a larger molecule. The resultant condensed molecule is a fused-insoluble structure known as a "cured" or "crosslinked" network.

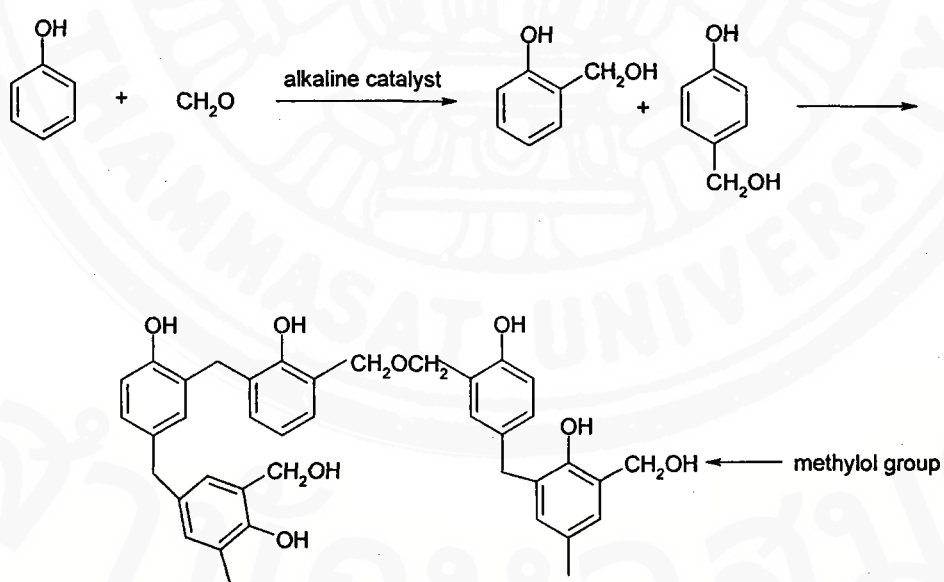


Figure 1.1 The synthesis pathway and structure of resol.

In contrast, novolac is produced from the condensation reaction of phenol and formaldehyde using an acid as a catalyst. The commonly used acid catalysts are HCOOH, halogenic acid (HX), oxalic acid, H_3PO_4 , H_2SO_4 , and CCl_3COOH . This novolac resin contains no reactive methylol groups in its molecule. (See figure 1.2) Therefore, upon heating it is unable to form a "crosslinked" network by itself. In order to cure a novolac, a curing agent must be added. Additionally, the original phenol to formaldehyde mole ratio plays an important role in synthesizing phenolic resins. A ratio of less than one must be applied to the preparation of resol, in order to provide a source of methylol groups. On the other hand, novolac does not contain methylol groups in its molecule so that excess formaldehyde is not necessary. Therefore, a phenol/formaldehyde molar ratio of greater than one is used.

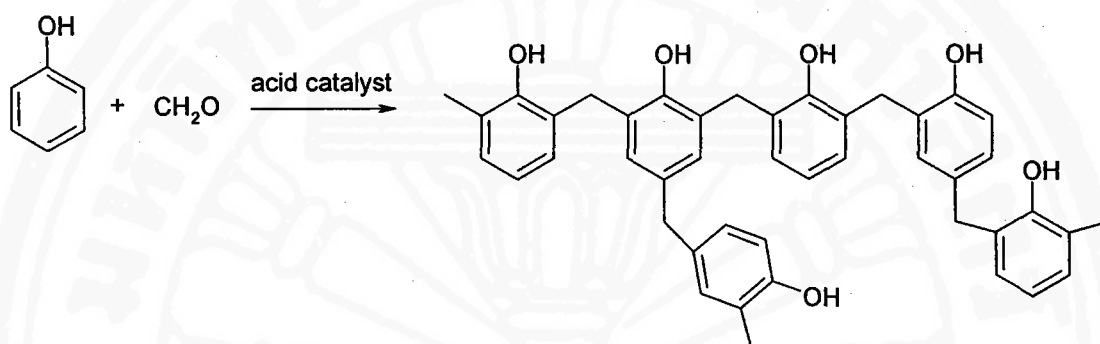


Figure 1.2 The synthesis pathway and structure of novolac.

Beside phenol, some mono-substituted phenol compounds can be used in synthesizing phenolic resins. Substituted phenols that can be used are p-cresol, p-phenylphenol, p-tert-butylphenol, p-tert-amylphenol, p-octylphenol, and bisphenol A. However, the resinous products from these reactions are low molecular weight materials and can not be cured by heating to form a "crosslinked" network. This is because these mono-substituted phenolic compounds have only reactive *ortho*-sites, unlike the normal phenolic resins that can react with formaldehyde at either *ortho*- or *para*- positions. The most common substituted-phenolic resin is p-cresol formaldehyde (PCF) resin, which its synthesis pathway is shown in figure 1.3.

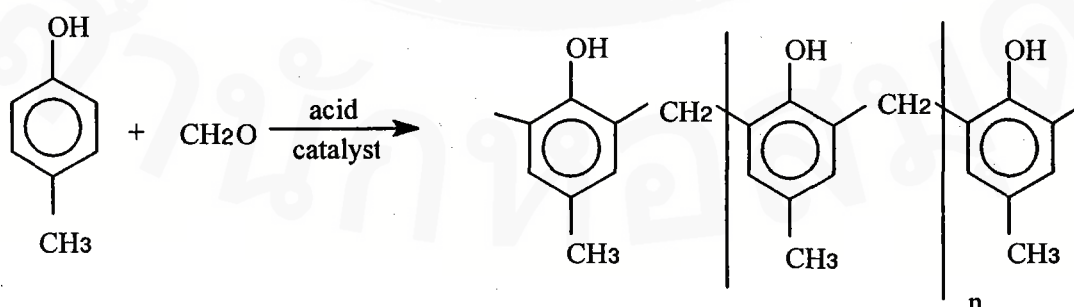


Figure 1.3 The synthesis pathway and structure of p-cresol formaldehyde (PCF) resin.

1.2 Characterizations of Phenolic Resins

There are several techniques used in characterizing phenolic resins. Among the most useful are chromatography, NMR, FTIR, and thermogravimetric analysis. Gel Permeation Chromatography (GPC) has been used to determine the molecular weight and molecular weight distribution of (uncured) phenolic resins. ^1H NMR and ^{13}C NMR along with FTIR have been used to study the structure of phenolic resins. FTIR spectra of resol and novolac are compared in figure 1.4. A major difference between the two spectra is observed at a peak at 1001 cm^{-1} , which represents the C-O stretching of methylol groups. The hydroxyl peak of the two samples indicates a difference in their molecular structure. The hydrogen bonded hydroxyl peak of resol (3302 cm^{-1}) is at lower wavenumber than that of novolac (3341 cm^{-1}), because resol contains both phenolic and aliphatic hydroxyl groups and the latter can form stronger hydrogen bonds. The peaks in the region lower than 900 cm^{-1} indicate that the phenolic rings are connected by a combination of ortho-ortho (o-o), ortho-para (o-p), and para-para (p-p) methylene bridges. Figure 1.4 also compares the FTIR spectra of novolac and the p-cresol formaldehyde (PCF) resin. The major difference is the hydrogen-bonded hydroxyl peak. The peak at 3235 cm^{-1} of the PCF spectrum indicates that much stronger hydrogen bonds occur in PCF than that in the phenol based novolac (and other phenolics previously studied in our laboratory). This is intriguing and probably due to a formation of intra-molecular hydrogen bonding, which results in an enhancement in the adhesive property of this polymer.

There are some minor controversies in assigning phenol bands in the region of 1300 cm^{-1} . However, on the basis of various studies, including deuteration experiments, the in-plane OH deformation should be assigned to the peaks in this region. The normal free OH bending occurs near 1250 cm^{-1} , and the associated OH bending falls in the range of 1300 cm^{-1} to 1400 cm^{-1} . Moreover, it has been found that associated OH bending band shifts to higher frequency with increasing strength of the hydrogen bonding.^{4,5} The relationship between the strength of the hydrogen bonds and the position of the in-plane hydroxyl deformation (dip(OH)) peak is well indicated in the FTIR spectra. The peak is found at 1360, 1374, and 1380 cm^{-1} for novolac, resol and PCF, which have hydrogen bonds that range in strength from the lowest to the highest, respectively.

GPC results show a number-average molecular weight of 1900, and 1300 g/mole for novolac and PCF, respectively, based on Polystyrene standards. PCF has a lower average molecular weight because of its lower number of reactive sites on the ring, even though the same reaction conditions were employed in the synthesis of the two resins. The thermal properties of the resins have been studied by DSC and the results are shown in figure 1.5. The resol cannot be used in the study since the resin does not show a glass transition temperature (T_g). Furthermore, the resin is self-hardening so that it forms a cross-linked network upon heating. However, novolac and PCF were studied and the glass transition temperatures (T_g) of 65 and $56\text{ }^\circ\text{C}$ were obtained, respectively. Novolac has a higher T_g because of two possible reasons, its higher molecular weight and its branched structure, which restricts the rotational freedom of the segments.

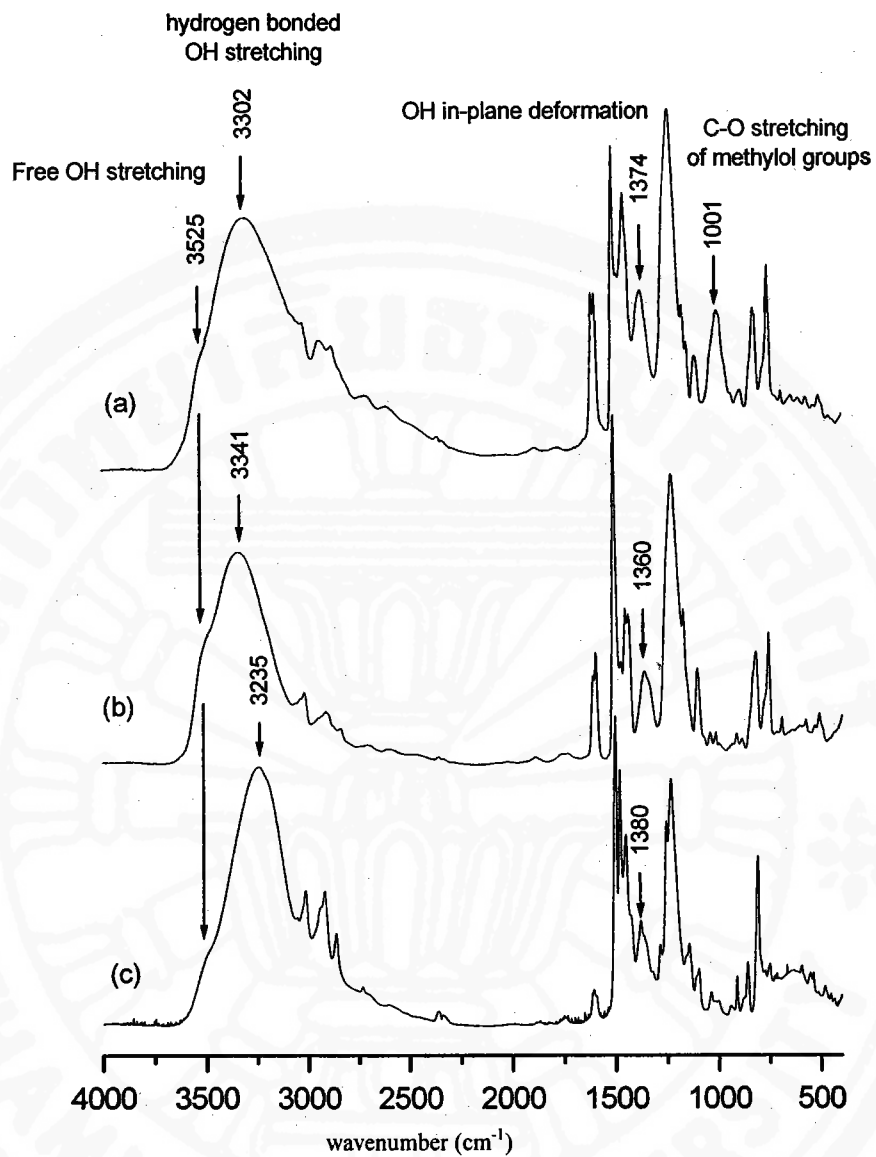


Figure 1.4 FTIR spectra of resol (a), novolac (b), and p-cresol formaldehyde resin (c).

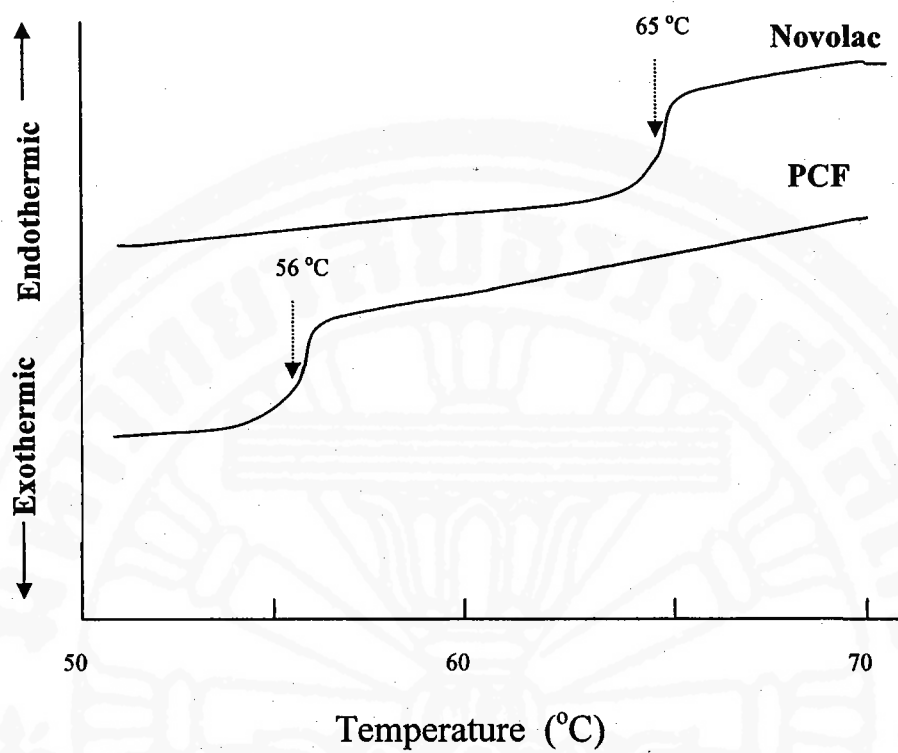


Figure 1.5 DSC thermograms of novolac and PCF.

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