
CHAPTER 13

**EXPERIMENT FOR
PHENOL-FORMALDEHYDE
RESIN**

1. INTRODUCTION

Resins are in general raw materials, for example for binders, curable molding compositions adhesives and coatings. They normally have a melting or softening range, are brittle in the solid state. Resin can be divided as natural resins and synthetic resins.

The most important synthetic resins are phenol-formaldehyde resins, urea-formaldehyde, melamine-formaldehyde resins, polyesters resins, silicone resins, ketone-aldehyde resins, epoxy resins, acrylic resins and alkyd resins.

They are usually thermoset type polymers. Thermoset resins are usually prepared as prepolymer and then in the second stage they are cross-linked by the effect of catalyst, heat and pressure. Phenolic resins are thermoset type polymers.

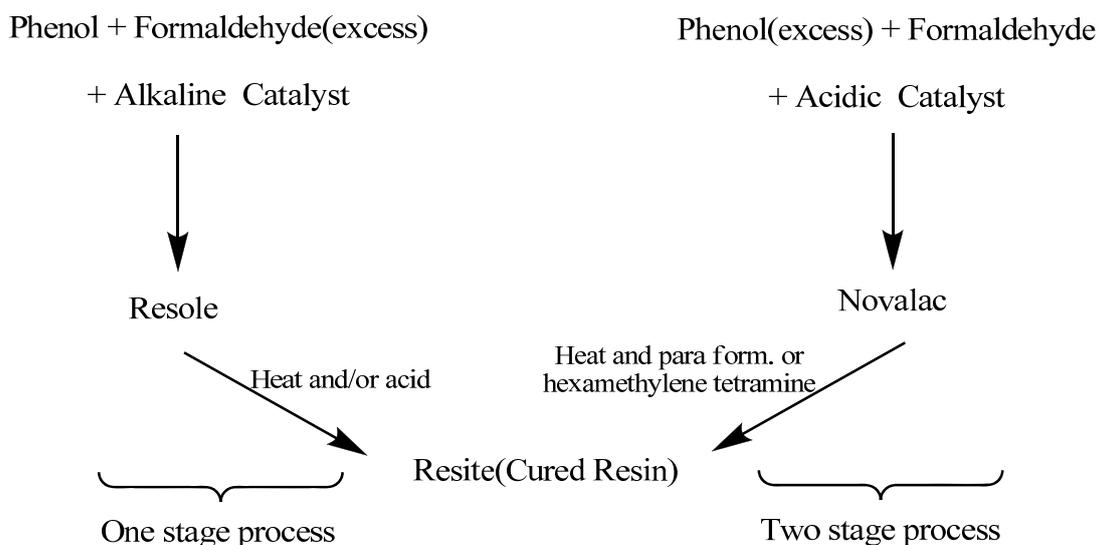


Figure 1: Phenolic Resin Processes

Phenolic resins are made by reaction of formaldehyde with phenol and substituted phenol. The products depend on the phenols used, the stoichiometric ratio of phenol to formaldehyde, and the pH during the reaction. Phenolic resins are of two main types. The resins resemble either the phenol alcohols or the dihydroxydiphenylalkanes in basic structure. If they are prepared with an excess of formaldehyde and an alkaline catalyst they will resemble the phenol alcohols and have methylol side or end groups. Such resins are often referred to as resoles. They are capable of being cured by the application of heat and acids, cure resulting through condensation of the methylol groups. By cooling the resin the reactions may be conveniently stopped, or at least effectively retarded, anywhere between the addition of the

formaldehyde and the final curing process. To resume reaction the temperature is raised or an acidic catalyst is added. Since there is no sharp break in these reactions such resins have been termed the one-stage resins. The majority of the one-stage resins employ formaldehyde as the aldehyde, although certain other aldehydes may be used. Formaldehyde is preferred because of its high reactivity and freedom from side reactions. On the other hand, if the phenolic resin is prepared with an acidic catalyst and less than a mole of formaldehyde per mole of phenol the resin will resemble a hydroxydiphenylmethane in structure, e.g. the chains are phenol ended. These resins, commonly referred to as novolacs, are permanently soluble and fusible and cure only upon the addition of curing agent. As the preparation of the novolac resin represents one process and the addition of the curing agent represents a separate and distinct process, resins based on a novolac resin and curing agents are referred to as two-stage resins. An outline of the two processes is given in Figure 1. Phenolic resins are used on a large scale in plastics and adhesives applications.

1.1. Resoles

Under alkaline conditions, the initial reaction product of phenol and formaldehyde is a mixture of ortho and para methylolated phenols. The methylolated phenols are more reactive with formaldehyde than the unsubstituted phenol resulting in the rapid formation of 2,4-dimethylolphenol and subsequently, 2,4,6-trimethylolphenol; the latter is the predominant product, with a large excess of formaldehyde and relatively short reaction time. With lower ratios (but still a molar excess) of formaldehyde to phenol and longer reaction times, formation of higher molecular weight resole phenolic resins is favored.

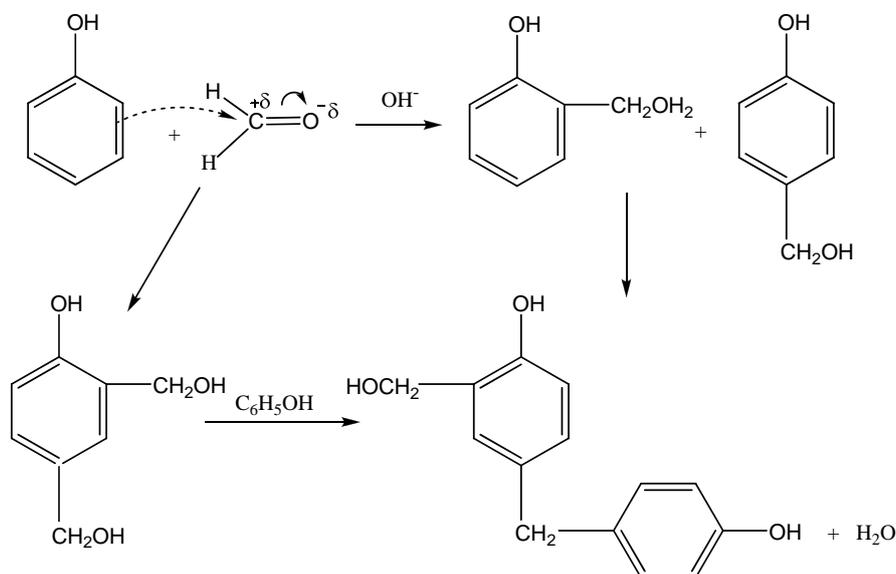


Figure 2: Resole

Polymerization occurs primarily by a methylol group on one phenol reacting at the ortho or para position of another phenol to form methylene bridge connecting the two phenols. Dibenzyloether bridges connecting two phenols also form by reaction of two methylol groups with each other. With excess formaldehyde, methylol groups are present on the terminal phenol groups of resole resins. Although not shown in the general structure some of the aromatic rings have three substituents.

Such phenol-based resole resins cross-link on heating and are used in adhesive and plastics applications. However, they are not suitable for coatings applications, primarily because their cross-link density is higher than appropriate for any coating. Furthermore, the package stability of the resins is limited. Resole phenolics useful in coatings applications are made from monosubstituted phenols with phenol. The use of substituted phenols reduces the potential cross-link density. There are two broad categories of such resins: (1) those that are soluble in alcohol and other low molecular weight oxygenated solvents, commonly called alcohol-soluble, heat-reactive phenolics; and (2) those that are soluble in vegetable oils and are called oil-soluble, heat-reactive phenolics.

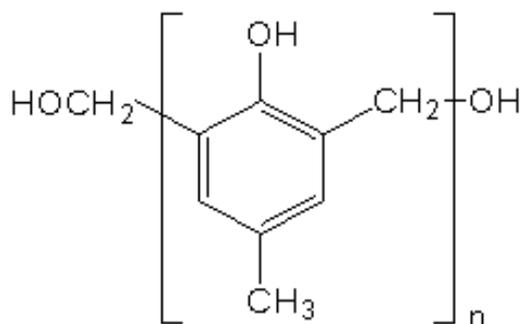


Figure 3: Resole Phenolic Resin (from p-cresol) – (Idealized Structure)

Alcohol-soluble, heat-reactive resole resins are prepared by reacting phenol, o- or p-cresol, and formaldehyde in the presence of a base catalyst at less than 60°C while removing water under vacuum. The catalyst neutralized, alcohol is added, and the salt resulting from catalyst neutralization is removed by filtration. Potential cross-link density is controlled by the ratio of formaldehyde to phenols and by reaction time.

Such resole phenolic resins are used in interior can coatings and tank linings. They require baking using an acid catalyst in order to cure in short times. To enhance flexibility and adhesion, they are commonly blended with low molecular weight poly(vinyl butyral) as a plasticizer. The films are resistant to swelling by oils such as encountered in canned fish and are completely resistant to hydrolysis. These resins and other heat-reactive phenolics discolor during baking, which restricts their usage to applications for which development of a yellow-brown color is permissible. These resins are also blended with epoxy resins in thermosetting coatings for applications such as primers and can coatings. The absence of hydrolysable bonds and generally excellent adhesion properties are their chief advantages.

Oil-soluble, heat-reactive phenolics are prepared by reacting a para substituted phenol, (e.g., p-phenylphenol, p-t-butylphenol, or p-nonylphenol) with somewhat less than 2 moles of formaldehyde per mole of substituted phenol. The resulting resole phenolics are cast from the reactor after neutralization of the catalyst. The resulting resole phenolics are solid, linear resins with terminal methylol groups. The most common use for such resins is to make varnishes with linseed oil and/or tung oil. However, since varnishes have, in large measure, been replaced by other vehicles, the consumption of these resins has declined markedly.

2. EXPERIMENTAL

2.1. Procedure

Into a three-necked flask, 0.1 mol of phenol and 0.2 mol of formaldehyde (formaline solution), were added and heated to 60°C while stirring then added was 1 ml of 20% NaOH in equal portions (kept at pH 9 by means of a solution of 20% w/v of NaOH). After 2h the reaction was completed. Then it was neutralized until the pH reached 6-7. The upper phase was decanted. It was then washed several times with water, and dried at 70°C under vacuum.

3. REFERENCES

- [1] **Wicks, Z.W., Frank, J.R., Jones, N., Pappas, S.P.**, (1999). *Organic Coatings Science and Technology*, 2nd Edition, John Willey.
- [2] **Armat, R., Bike, S.G., Chu, G., Jones; F.N.**, (1996). *J. App. Polym. Sci.*, 60, 1927.
- [3] **Martin, R.W.**, (1999). *The Chemistry of Phenolic Resins*, John Willey.
- [4] **Manfredi, L.B., Riccardi, C.C., De la Olsa, O., Vazquez; A.**, (2001). *Polym. Int.*, 50, 796-802.
- [5] **Higuchi, M., Urakawa, T., Morita M.**, (2001). *Polymer*, 42, 4563.
- [6] **Shipp, D.A., Solomon, D.H.**, (1992). *Polymer*, 38 (16), 4229.
- [7] **Kaledkovski, B., Hepler J.**, (2000). *Polymer*, 41, 1679.