Analysis of Synthesis of General-Purpose Phenolic Resin and Its Curing Mechanism

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Abstract
Based on analysis of existing problems related to general-purpose phenolic resin and extensive laboratory experimental studies, a synthetic method for general-purpose phenolic resin was determined. Its curing mechanism and the influencing factors of curing rate were investigated. Commonly used curing agents and corresponding dosage for phenolic resin synthesis were also identified. This paper provides a reference for research on phenolic resin modification.

Key words: Phenolic resin; Synthesis; Curing mechanism; Influencing factors

INTRODUCTION
Phenolic resin is a synthetic resin that is mainly used in the adhesive industry. The relative molecular weight of phenolic resin is approximately 700–1,000. It is formed as a polycondensation of phenol (or cresol, xylenol, and resorcinol) and formaldehyde under acid or basic catalyst. Thermoset phenolic resin and thermoplastic phenolic resin could be formed by using various phenol/formaldehyde ratios and catalysts. Thermoset phenolic resin (or resole) is the reaction product of phenol and formaldehyde (dosage < 1 mol/L) under the existence of basic catalysts (For example, ammonia water, sodium hydroxide, potassium hydroxide, barium hydroxide, calcium hydroxide, and ethylamine), which generally could be dissolved in ethyl alcohol and acetone. Water-soluble phenol-formaldehyde resin could be prepared, such as 2,122 phenolic resin, 2,127 phenolic resin, 264 phenolic resin, and 219 phenolic resin, to reduce price and pollution. Thermoplastic phenolic resin (or novolac), such as 3,201 phenolic resin and 2,123 phenolic resin, is the reaction product of phenol and formaldehyde (dosage > 1 mol/L) under the existence of acid catalysts (For example, hydrochloric acid, sulfuric acid, and oxalic acid). It is soluble in ethyl alcohol and acetone.

About 20% of free phenol remains in phenolic, and is harmful to people’s health who are exposed to this chemical. Moreover, the existence of acid or basic catalyst decreases the resin bonding strength over time. Given these limitations, general-purpose phenolic resin was synthesized through numerous laboratory tests. This process improves gelation speed, free phenol content, and water content, and has potential for widespread application.

1. TEST MATERIALS, INSTRUMENTS, AND METHODS

1.1 Test Materials and Instruments
1.1.1 Main Test Materials
(a) Phenolic resin: Used phenolic resins were collected from Laizhou Resin Plant and prepared in a laboratory.
(b) Curing agent: Used curing agent were prepared by a compound or chemical reagent in the laboratory.
(c) Other reagents or materials: HMT, phenol, formaldehyde, oxalic acid, and caustic soda are chemical reagents.

1.1.2 Main Test Instruments
DV-I + Viscometer (USA).
Electric-heated thermostatic water bath (Longkou Sast Instrument Company, China).
Circulating water multi-use vacuum pump (Zhengzhou Changcheng Technology & Trade Co. Ltd., China).

Resin reaction still, stirrer, thermometer, second chronograph, and general glassware and vessels.

1.2 Main Testing Method

1.2.1 Resin Gelation Time (Polymerization Rate)

A certain amount of test samples were weighed and added with HMT (thermoset resin was not added). The mixture was then placed in a mortar and ground into powder. Then, 1 g of powder was placed in a heating plate square groove with adjusted temperature (150 ± °C). A piece of glass was used to shake the powder in order to melt it. The time from complete melting to free filamentation of resin was recorded by a stopwatch. The melted resin was stirred continuously with a glass rod, and the glass rod was lifted from time to time to observe whether the resin had stopped filamentation. Two tests were conducted and the mean time was taken as the polymerization rate (gelation time) of the sample.

1.2.2 Resin Viscosity

A certain amount of resin samples were weighed and placed on a viscometer to test resin viscosity. A total of three tests were conducted on each sample and the mean value was considered as the final viscosity rate.

2. SYNTHESIS OF GENERAL-PURPOSE PHENOLIC RESIN

Many types of phenolic resins exist, but all of them have limitations. Therefore, studying the modification of phenolic resin is necessary. Aside from improving the performance of the resin by adding other materials, modification has other important aspects such as adding sequence, reaction temperature, reaction return time, and vacuum degree evacuation. As a result, the synthesis method of general-purpose phenolic resin was determined through a laboratory test.

2.1 Synthesis of Common Thermoset Phenolic Resin

In the experiment, 50 g of phenol and 25 ml of 40% NaOH solution were added into a flask with four mouths. The mixture was stirred and was maintained for 20–30 min at 40–45 °C. The temperature was controlled at 42–45 °C, and 50 ml formaldehyde was added within 30 min. Then, the temperature was increased gradually until it reached 87 °C at 1.5 h. The temperature of the reactant was then increased to 87 °C to 94 °C within 25 min. This temperature was maintained for 20 min and was then decreased to 82 °C for 15 min. Then, 10 ml formaldehyde and 10 ml water were added, and the temperature was increased to 90–92 °C. After reacting for 20 min, the samples were collected to test their viscosity until they achieved a satisfactory viscosity rate. Finally, the samples were cooled to 40 °C and the products were collected.

2.2 Synthesis of Common Thermoplastic Phenolic Resin

As part of the experiment, 130 g of phenol (1.38 mol), 13 ml of water, 92.4 g of 37% formaldehyde solution (1.14 mol), and 1 g oxalate dihydrate in a 1,000 ml reaction were further added. The mixture was stirred and heated, and was backflowed for 30 min. Then, 1 g oxalate dihydrate was added and another 1 h backflow was conducted. Thereafter, 400 ml water was added. After the mixture was cooled, it was kept static for 30 min. Upper water was siphoned off and condensation was changed to vacuum distillation. The mixture was heated and the temperature was increased to 120 °C under 6.67–13.34 kPa until it reached the required level. Then, 140 resin was collected, whose productivity was limited within 105% (calculated according to phenol mass).

3. CURING MECHANISM OF PHENOLIC RESIN

First-order thermoset phenolic resin is a product of polycondensation when it is controlled within a certain degree. Therefore, appropriate reaction conditions could facilitate the process of polycondensation to form a shaped polymer. Second-order thermoplastic phenolic resin forms a linear thermoplastic resin because of the inadequate dosage of formaldehyde during the synthesis. However, it has unreacted active sites in resin molecules. Thus, polycondensation could continue and form shaped polymers that could react with active sites (or curing agent) through the addition of formaldehyde.

3.1 Curing of Thermoset Phenolic Resin

Curing performance of the first-order resin is mainly determined by phenol/formaldehyde ratio and appropriate degree of system functionality. As previously introduced, formaldehyde is a di-functional monomer. To obtain resin that could be cured, the degree of functionality of phenol must be higher than 2. In three-functional phenols, phenol, methylyphenol, and resorcinol are the most commonly used raw materials. A mixture of three-functional phenol and di-functional phenol can also generate curing resin. The phenol/formaldehyde ratio (mass ratio) for preparing the first-order resin can reach as high as 15:1 when the curing resin achieves maximum physical performance. The first-order thermoset phenolic resin can be cured under both heating conditions and acid conditions.

3.1.1 Thermocuring of Thermoset Phenolic Resin

i. Principle of thermocuring

During thermocuring of the first-order resin, methylene bond and ether bond are formed simultaneously. The methylene bond/ether bond ratio in the curing structure is related to the number of hydroxymethyl in the resin, acid-base property of the system, curing temperature, and number of reactive hydrogens on the phenol ring. If
the curing temperature is lower than 160 °C, generation of dibenzyl ether is a highly important reaction for the first-order resin formed by substituted phenols. This reaction may also occur in resin synthesized of three-functional phenols, but it is less important in such a case. If the resin is alkaline, it mainly produces a methylene bond. Under acid conditions, the methylene and ether bonds are generated simultaneously, but under strong acid conditions, a methylene bond is produced.

Under high temperature (>170 °C), the dibenzyl ether bond is unstable and could further react. Nevertheless, the methylene bond is stable and does not break when the temperature is lower than that of complete resin decomposition. Under neutral conditions, the methylene bond is mainly the connection pattern in the curing structure of the first-order resin synthesized from three-functional phenols. When the curing temperature ranges between 170~250 °C, the polycondensation of the second stage is highly complicated. At this point, dibenzyl ether bonds decrease quickly, whereas methyl bonds increase significantly. Additionally, methenyl benzoquinone as well as their polymers and redox products are generated. The structure of the 4-methylene-2, 5-cyclohexadiene-1-ketone or the 6-methylene-2, 4-cyclohexadiene-1-ketone generated during the curing process is shown as chemical Equation (1):

\[ \text{Equation (1)} \]

ii. Influencing factors of thermo curing rate

(a) Phenol/formaldehyde ratio for resin synthesis: The reaction rate of the first-order thermoset resin during curing is related to formaldehyde dosage. With the increase of formaldehyde content, the gelation time of resin shortens (Seen Figure 1).

(b) Alkalinity or acidity: the thermoset property of the first-order resin is significantly influenced by the alkalinity or acidity of the system. When the curing system has pH = 4 as neutral point, the curing reaction is extremely slow. Increasing the alkalinity causes fast gelation and increasing the acidity causes extremely fast gelation.

(c) Temperature: if the curing temperature increases 10 °C, the gelation time of the first-order resin will shorten to about half of its original length.

iii. Thermocuring process

This process is often conducted when using thermocuring phenolic resin to prepare glass-fiber reinforced composite materials. The final curing temperature is often controlled at approximately 175 °C. Moulding pressure is often controlled within 6.5–50 MPa according to requirements.

3.1.2 Acid-Curing of Thermoset Phenolic Resin (Curing Under Normal Temperature)

When the first-order phenolic resin is used as adhesive, it has to be cured under low temperature and even under room temperature. For this purpose, appropriate inorganic or organic acid could be added into the resin. These inorganic or organic acids are called acid-hardening agents in industrial use, including hydrochloric acid or phosphoric acid (they can be dissolved into glycerinum or glycol), p-toluenesulfonic acid, phenolsulfonic acid or other sulfoacid. The performance rates of corresponding sulfoacids are listed in Table 1.

During acid curing of the first-order phenolic acid, the main reaction involves generation of a methylene bond between resin molecules. Dienzyl ether could also be generated under small dosage of lactic acid, low curing temperature, and high hydroxymethyl content in resin molecules. Acid curing of the first-order phenolic acid is characterized by violent reaction and release of tremendous heat. The extreme heat that is released during polycondensation under the catalysis effect of phenol and aldehyde helps in preparing phenolic resin with spontaneous bubbling behavior. Reaction heat is mainly released from the reaction between phenolic alcohol and phenol or the phenolic alcohol itself. Moisture condensation causes the bubbling of resin. Heat-release solution increases the resin temperature and intensifies the curing reaction.

Acid curing of the first-order phenolic resin is effective under a low pH level. The first-order resin is highly stable when pH = 3–5. For various types of first-order resins, the pH range of the highest stability is related to the phenol type used in resin synthesis and curing temperature. First-order resins synthesized
from resorcinol achieve the highest stability when pH = 3, and those synthesized from phenol reach the highest stability when pH is approximately 4. Obviously, the curing reaction when pH < 3 is catalyzed by acid, but that under high pH (>5) is catalyzed by alkaline.

Table 1
Performance Rates of Sulfoacid Hardening Agents

<table>
<thead>
<tr>
<th>2-Chloroethyl p-toluensulfonate</th>
<th>Benzene sulfonyl chloride</th>
<th>Ethyl sulfate</th>
<th>Petroleum sulfonic acid</th>
<th>NL curing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Gray while crystal</td>
<td>Colorless liquid</td>
<td>Brown viscous fluid</td>
<td>Dark gray viscous fluid</td>
</tr>
<tr>
<td>Smell</td>
<td>Frowzy</td>
<td>Pungent</td>
<td>Odourless</td>
<td>Odourless</td>
</tr>
<tr>
<td>Acidity</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Curing speed</td>
<td>Slow</td>
<td>Relative quick</td>
<td>Quick</td>
<td>Moderate</td>
</tr>
<tr>
<td>Reference dosage</td>
<td>10–12</td>
<td>8–10</td>
<td>8–15</td>
<td>6–8</td>
</tr>
<tr>
<td>Curing performance</td>
<td>Good</td>
<td>Good</td>
<td>Bad</td>
<td>Common</td>
</tr>
<tr>
<td>Characteristics and applications</td>
<td>It is dissolved or filled in advance. The mixture cures slowly but is used widely.</td>
<td>It is easy to mix evenly and is easy to use. It smells good and is widely used.</td>
<td>Short pot life, slight smell, several applications</td>
<td>Non-toxic, easy to use, limited resources, few applications</td>
</tr>
</tbody>
</table>

3.2 Curing Reaction of Thermoplastic Phenolic Resin

3.2.1 Curing Reaction
Thermoplastic phenolic resin, that is, the second-order resin, is soluble and fusible. It can only cure when curing agents (For example, paraformaldehyde and HMT) are added to react with active sites on the phenol ring in the resin molecules. Thermoset phenolic resin can also be used for curing second-order resins because hydroxymethyl in thermoset phenolic resin molecules could react with active hydrogens on the phenol ring of thermoplastic phenolic resin to form three-dimensional net-structured products. HMT is the curing agent that is mainly used with the thermoplastic phenolic resin. This agent has such advantages as quick curing, preparation of stable curing structure, absence of water discharge during curing, and good electrical performance of workpieces. The affixture of HMT and formaldehyde resembles white crystals and sublimate quickly at 150 °C. Its molecular formula is (CH₃)₃N₄ and the structure is presented in chemical formula (2). HMT decomposes into dimethyl carbinol and formaldehyde once its temperature exceeds 100 °C, which enables a crosslinking reaction with phenolic resin.

![Chemical structure of HMT](image)

3.2.2 Influencing Factors of Curing Reaction
(a) HMT dosage: HMT dosage significantly affects the gelation speed, curing rate, and heat resistance of second-order resins. An inadequate HMT dosage reduces the heat resistance of the product, while an excessive HMT dosage deteriorates both the heat resistance and electrical performance of the product. Generally, the HMT dosage of resin is 6%~14% and the optimum dosage is approximately 10% (Figure 2).

(b) Free phenol and water contents in resin: Common first-order resins contain a small amount of free phenol and water, which could affect gelation time. With the reduction of free phenol and water contents, gelation slows down. The effect of water content on the gelation time is shown in Figure 3. When the water content exceeds 1.2%, its effect is minimal. The effect of free phenol content on the gelation time is shown in Figure 4. The gelation time is extremely short when the free phenol content exceeds 7%~8%.

![Figure 2](image)

Figure 2
Effect of HMT Dosage on Gelation Time of Phenolic Resin

(d) Curing process: Pressing temperature of phenolic products is 150 °C~175 °C and the pressure is generally within the 30~40 MPa range. Owing to different curing conditions, various aspects of the first-order and second-order phenolic resins are emphasized in industrial applications. The former is mainly used as coating, adhesive, and matrix of composite materials, and the latter is mainly used as moulding pressing powder.

**CONCLUSION**

(a) The synthetic methods of general-purpose phenolic resins and their notes are determined through tests.

(b) The thermocuring process and principle of general-purpose thermoset phenolic resin as well as the influencing factors of curing rate are discussed.

(c) The thermocuring principle of general-purpose thermoplastic phenolic resin is analyzed. The effects of HMT dosage, free phenol content, water content, and curing temperature on thermoplastic phenolic resin are investigated through experiments.

**REFERENCES**


