

Study on the Curing Behavior of Resol. IV. Comparison of the Curing Behavior of Resols Prepared with either Sodium Hydroxide or Barium Hydroxide

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Synopsis

Curing behaviors of two kinds of resols prepared by the reaction of phenol (1 mol), formaldehyde (1.2 mol), and either sodium hydroxide (0.02 mol) or barium hydroxide (0.01 mol), were examined at 120°C by means of Curelasterometer, IR spectroscopy, THF extraction, and GPC. Gelling and curing speeds of the resol prepared with barium hydroxide as catalyst (BR) were faster than with sodium hydroxide (NR). The amount of hydroxymethyl groups in BR also decreased more rapidly with an increase in the cure time than that in NR by IR spectrometry. Similar results were confirmed by THF extraction and GPC. It is recognized in the curing of both resols that relatively higher molecular weight compounds gel rapidly and that, after major components in the resol have changed to gel, low molecular weight compounds still remain in the resol as sol state. It is inferred from GPC that NR differs from BR in the molecular weight of the compounds which exist prior to gel formation, namely, the molecular weight of the compounds in BR is smaller than that in NR.

INTRODUCTION

The composition of resol varies with the kind of catalyst used in the preparation of resol.¹⁻⁴ When an alkaline earth metal hydroxide is used as catalyst, the ratio of ortho/para substituents in hydroxymethyl phenols becomes larger than that in resol prepared with alkali metal hydroxides.

On the other hand, the curing speed of the resol containing more ortho-substituted hydroxymethyl phenol (high-ortho type resol) prepared with alkaline earth metal hydroxide is faster than that of the resol containing the more para-substituents (high-para type resol) prepared with alkali metal hydroxide.⁵

In examining the added effect of cure catalysts such as alkali metal or alkaline earth metal hydroxides on curing behavior of resol, we reported previously that the larger the ion radius of the alkali metal hydroxides and the alkaline earth metal hydroxides, the more the cure acceleration effect for the resol becomes, and that barium hydroxide is the most effective catalyst of the hydroxides used.⁶

The object of this paper is to understand the relation between the kind of catalyst used in the preparation of resols and the curing behavior of the

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resols. In this experiment, sodium hydroxide and barium hydroxide are chosen as a typical alkali metal hydroxide and alkaline earth metal hydroxide, and curing behavior of the resols has been compared and examined by means of a Curelastometer,^{6,7} THF extraction, IR spectroscopy, and GPC. Some studies on resol have been reported by means of GPC; the objects of the studies were mainly quality control, for example, to clarify the relation between the conditions of the resol preparation and the molecular weight distribution.^{8,9} There were few studies on cure behavior of resol using GPC.

Molecular weight distribution of resol became wider with curing until THF insoluble matter appeared, and, after that, molecular weight distribution of THF soluble parts in resol became narrow with curing. Though it is interesting to study the curing behavior of resol using GPC, it is difficult to examine the behavior quantitatively, because the compounds and isomers which are contained in resol are too many to be able to identify the compounds which correspond to each peak in gel permeation chromatogram. Since it is expected that useful information will be obtained on the curing behavior of resol by means of GPC, in this paper, the difference of the curing behavior of both resols is discussed by comparing the gel permeation chromatogram patterns of THF soluble matter semiquantitatively.

EXPERIMENTAL

Resol Preparation

Phenol 188 g (2 mol), 37% formalin 195 g (2.4 mol), and either 0.04 mol of sodium hydroxide or 0.02 mol of barium hydroxide were charged in a 1-L three-necked flask fitted with a stirrer, a thermometer, and a reflux condenser. The mixture was brought to reflux in 40 min, held at reflux for 1 h, cooled, and then dehydrated under 30 mm Hg until the temperature of the mixture reached 80°C. The resols that were prepared with either sodium hydroxide or barium hydroxide will hereinafter be abbreviated NR or BR, respectively. The amount of free phenol in NR was 12.4 and 15.3% in BR, and pH values were 9.2 and 8.5, respectively. Gel permeation chromatograms of the resols are shown in Figure 1.

Measurement of Curing Behavior

Measurement by Curelastometer

The sample for Curelastometer was prepared by mixing 40 g of wood flour and the resol in which solid content of 100 g was included. Measurements of curing behavior were carried out with a Curelastometer II (Japan Synthetic Rubber Co.). The measurement and evaluation of the results were done by the same method described previously.⁶

Measurement by IR Spectroscopy

About 4 g of resol was put between two sheets of aluminum foil, and then pressed to 1 mm thickness by the hot plates of a Diskcure Tester¹⁰ the temperature of which was precisely controlled at a set value. After a certain

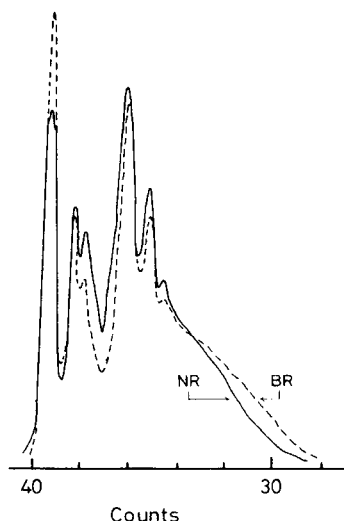


Fig. 1. GPC charts of NR and BR.

cure time, the cured resol between foils was cooled to room temperature as soon as possible, and when the cured resol was solid, it was pulverized to pass through a 100-mesh sieve. About 3 mg of the sample and 250 mg of KBr were mixed, and the sample was pressed into tablet form. The IR absorption spectrum of the cured resol was measured by means of a Shimadzu IR Spectrometer 27G.

THF Extraction Test

The glass sealed tube, in which 150 mg of fine pulverized cured resol described above and 5 mL of THF were contained, was heated in a water bath for 80 min at 60°C; then the tube was opened, and the mixture was filtered. The filtrate was used as a sample for GPC. The insoluble resin was dried after washing with fresh THF and weighed.

GPC Measurement

GPC was performed on 7.9×500 mm columns (arrangement: HSG 50-40-30-15, 2 m) with THF as the eluent at 1 mL/min by a Shimadzu-DuPont Model 830 Chromatograph, and a 1 elution count in chromatogram corresponded to the elution volume of 1.95 mL. Since the samples for GPC measurement were filtrates (THF extracts) described above, the area of GPC curve was approximately proportional to the amount of resin which was contained in the filtrate. When the amount of insoluble matter in the heated sample increased, the area of the GPC curve decreased.

RESULTS AND DISCUSSIONS

Curing Behavior of NR and BR by Means of Curelasterometer

The curing behavior of samples was measured over the temperature range 120–170°C by means of a Curelasterometer (Fig. 2). The curing speed of BR is faster than that of NR, especially in gelling behavior (t_1). The curing

behavior of both resols indicated results analogous to those shown in a previous paper,⁶ in which the same hydroxides were used as curing catalysts. Therefore, the hydroxide added as curing catalyst has a similar effect on the curing of the resol as the hydroxide which is used in the preparation of the resol. Table I shows the apparent activation energies that were calculated from the slopes of the lines in Figure 2.

Though a remarkable difference between both resols is not found in Table I, there is a little difference in their curing behavior in Figure 2: BR gells faster, and the difference of gelling and curing behavior between both resols increases with a lower curing temperature.

The results obtained in this and the previous paper are in agreement. The following examinations were done to properly understand the difference between the curing behaviors of the resols.

THF Extraction

Relations between the percent of THF extraction of both resols cured at 120°C and cure time are shown in Figure 3. Though NR is still soluble up to 13 min, insoluble material appeared in the BR heated for 5 min. In addition, BR cures more rapidly than NR.

Curing Behavior of NR and BR by Means of IR Spectroscopy

The amount of hydroxymethyl group in a resol decreases as the cure reaction proceeds.¹¹ The change in the amount of the hydroxymethyl group in resol was evaluated by the ratio of the absorbances (D_{1010}/D_{1610}). Figure 4 shows the relation between the ratio of the sample and cure time. This figure shows the following results: (i) The amount of hydroxymethyl group in BR as-prepared is larger than that in NR; (ii) the rate of the decrease

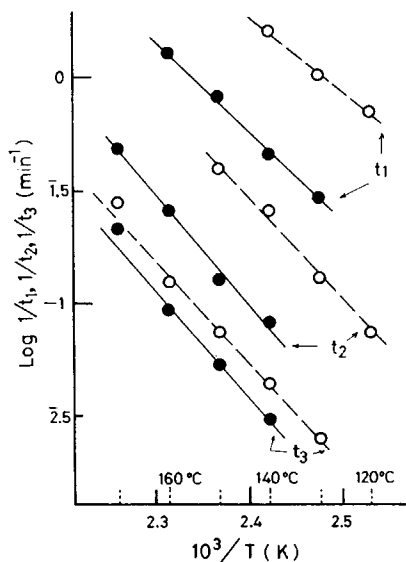


Fig. 2. Arrhenius plot for curing speed of NR and BR: (●) NR; (○) BR.

TABLE I
Apparent Activation Energy of Curing Behavior of NR and BR

Resol	t_1 (kcal/mol)	t_2 (kcal/mol)	t_3 (kcal/mol)
NR	17.2	20.5	21.1
BR	14.0	18.4	20.0

in hydroxymethyl group in BR is faster than that in NR, that is, curing speed of BR is faster than that of NR; and (iii) the absorbance ratios of the samples in which THF insoluble matter appeared in both resols resemble each other in the range from 0.5 to 0.6.

Concerning the reactivity of hydroxymethyl phenols, 2-hydroxymethyl- and 2,6-bis(hydroxymethyl)phenol that are unsubstituted, in the para position are more reactive than the analogous 4- and 2,4-compounds.¹² In hydroxymethyl phenols, the para position is more reactive than the others. The ratio of ortho/para hydroxymethyl groups in the resol that is prepared by use of alkaline earth metal hydroxides is larger than that of alkali metal hydroxide catalyst.¹⁻⁴

The difference in the curing behavior between both resols is due to the following: (i) The substitution modes of hydroxymethyl group on phenol nucleus are different in both resols; (ii) both the effect and the behavior of barium hydroxide on cure acceleration of resol differ from that of sodium hydroxide.⁶

GPC

In comparing the curing behaviors of NR and BR by means of GPC, the change in the chromatogram pattern of the THF extract on the curing was examined. The chromatogram of resol just before the THF insoluble matter appeared (the widest molecular weight distribution) was divided into nine sections along elution volume direction (Fig. 5). As the area of each section changed with cure time, each area was measured and related to cure time, and then the difference in the changing behavior of the area with cure time between both resols was examined.

In Figure 5, section A is phenol, B is a mixture of 2- and 4-hydroxymethyl phenol, and C is a mixture of 2,6- and 2,4-bis(hydroxymethyl)phenol, 2,4,6-

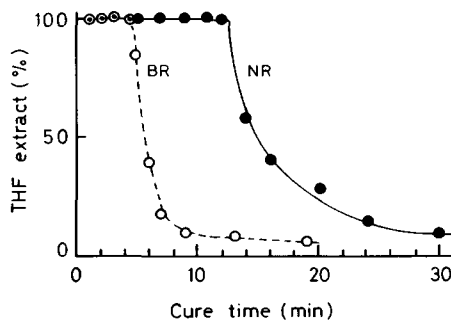


Fig. 3. THF extraction of NR and BR cured at 120°C.

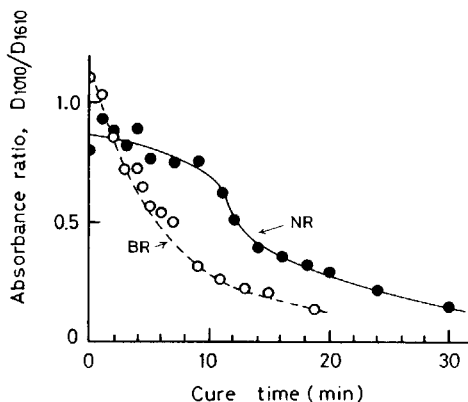


Fig. 4. Change in the absorbance ratio and cure time.

tris(hydroxymethyl)phenol, and derivatives of dihydroxy diphenyl methane.⁸

The area of each section (A-I) (Fig. 5) varies with cure time (Figs. 6 and 7). The asterisk (*) on each curve in the figures indicates the time when THF-insoluble matter appeared in both resols, respectively.

The amount of unreacted phenol in BR was much more than that in NR. This was noted by comparing the area of section A of both resols. Though the amount of phenol in BR decreased more rapidly than that in NR as the curing time proceeded in early curing period, after THF-insoluble matter began to appear in BR, the rate became slower, and then the consumption of phenol in both resols became similar.

Comparing the area of each section in both resols for about the first 5 min, at that time THF-insoluble matter appeared in BR, each area of B, C, D, and E of NR was larger than those of BR. In higher molecular weight sections such as F, G, and H, each area of the sections of BR series was larger than that of NR. When THF extracts of both the resols decrease to 10% respectively (Fig. 3, NR 30 min, BR 10 min), each area of sections

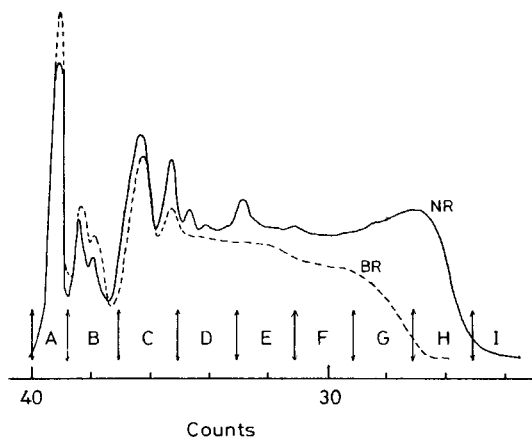


Fig. 5. GPC charts of widest molecular weight distribution and the divided sections.

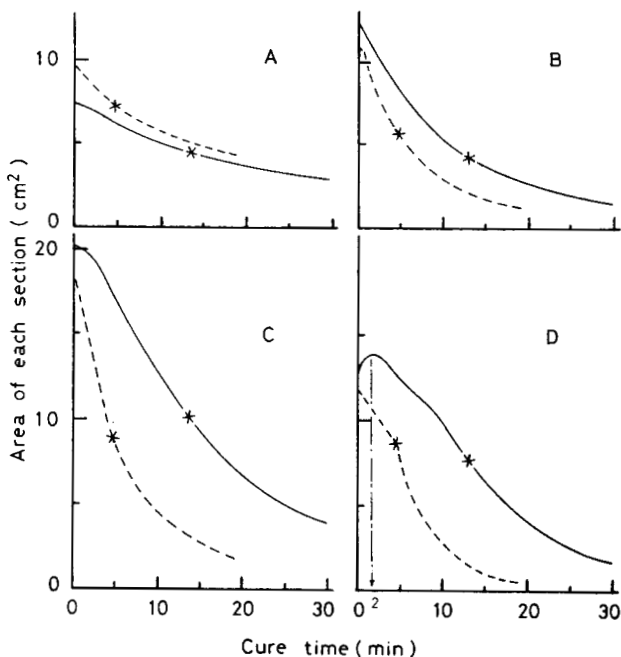


Fig. 6. Relation between area of each section (A-D) on GPC charts of NR and BR and cure time at 120°C: (—) NR; (---) BR.

A-D still remains over 10% of their initial values. After THF-insoluble matter appeared, each area of sections F-H decreased rapidly. In the NR series, each area of sections F-H decreased rapidly after THF-insoluble matter appeared. However, in BR, this phenomenon was already observed in section D. The compounds, which corresponded to the decreased area, would be due to THF-insoluble matter.

There are maximum values in sections D-H (Figs. 6 and 7); the time at

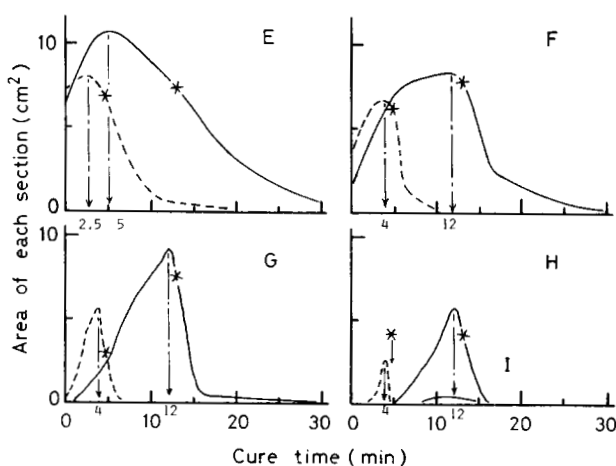


Fig. 7. Relation between area of each section (E-I) on GPC charts of NR and BR and cure time at 120°C: (—) NR; (---) BR.

each maximum value becomes longer as the section changes from D to F, and, then, the times saturate to 10 min (NR) and 4 min (BR), respectively. However, times are shorter than those measured when THF-insoluble matter appeared in both NR and BR. In sections E-I, which are relatively high molecular weight regions, the following phenomena are observed: Comparing both resols, the areas of the sections of BR are smaller than that of NR, and this tendency becomes outstanding with increasing molecular weight. Section I, which contains the highest molecular weight compounds, cannot be found in BR. Therefore, the molecular weight of the compounds in BR in the THF-insoluble fraction is smaller than that of the compounds in NR.

It is generally considered that the low molecular weight compounds, such as hydroxymethyl phenols, predominantly react with each other to produce a little larger molecular weight compound in the curing process. The molecular weight of the compound becomes larger and larger by step growth polymerization. Finally, the compounds change to insoluble crosslinked matter. Consider the curing behavior of both resols from the results described above: Relatively high molecular weight compounds having more functional groups than low molecular weight compounds are more reactive than low molecular weight compounds, so that the former reacts with each other predominantly to change the THF insoluble matter. Low molecular weight compounds such as phenol and hydroxymethyl phenols are not in the crosslinked matter. The results suggest that it is not suitable to use the resol which contains a large amount of low molecular weight compounds such as phenol and hydroxymethyl phenols for preparation of laminates or similar products. Such compounds left in the products may cause deterioration of electrical properties and the generation of a phenolic odor.

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