

The Curing Behavior of Resol. III. Effect of Alkali Metal Hydroxides and Alkaline Earth Metal Hydroxides as Catalyst for the Cure of Resol

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Synopsis

The effect of the addition of cure catalysts on the cure acceleration of ammonia free resol was investigated by means of Curelasmeter. The resol which was prepared by the reaction between phenol and formaldehyde with molar ratio 1:1.2 in the presence of NaOH (0.02 mol to phenol) was neutralized with HCl. Catalyst selected from LiOH, NaOH, KOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂ was added to the resol, and curing behavior of the resol was examined. Both alkali metal hydroxides and alkaline earth metal hydroxides accelerate the curing of resol. The cure acceleration effect of barium hydroxide is the largest. In the relation between the kinds of catalysts and the cure acceleration effect, the larger the ion radius of catalyst the faster the cure of resol. Cure speed of the resol containing either sodium hydroxide or barium hydroxide as a curing catalyst increases with an increase in the amount of catalyst. Apparent activation energies of curing behavior of the resols containing the cure catalysts were in the range 17.0–21.3 kcal/mol.

INTRODUCTION

Resol and novolac as intermediates of phenolic resin are made readily from the reaction of phenol and formaldehyde, and the former is prepared in the presence of basic catalyst.

Resol is widely used in many applications such as plywood, particle board, laminate, and moldings, because of its easy processability, good adhesive property, high performance of the products made from it, and relatively low cost. To obtain products with good properties, the curing behavior and acceleration of cure are also important.

Resol structures contain methylene, dimethylene ether linkages, and hydroxymethyl groups (methylol groups). The composition of resol varies with the kinds of basic catalysts that are used in its preparation.¹⁻⁴ Namely, the ratio of the ortho/para substituents (o/p) in the resol increases with a decrease in basicity of the catalyst used in the preparation of the resol. Curing behavior of resol varies with the composition of resol and both the kind and amount of cure catalyst added.^{5,6} Acid and base accelerate the cure of resol,⁷⁻¹⁰ But very few papers have been published on the effect of the addition of basic catalyst on the curing behavior of resol, especially on

the relation between the basicity of the catalysts and their cure acceleration effects.

There are many methods of measuring the curing behavior of thermosetting resins from gelling to curing. Some of them are suited for measuring the curing behavior of polyaddition type resins. In polycondensation type polymers, the volatile, low molecular weight byproducts are removed as the faster curing reaction proceeds. Therefore, it is important to choose a suitable method for measuring the cure behavior of polycondensation type resin. Furthermore, it is difficult to obtain the reproducible results of cure behavior, because resol often foams in curing. Curelasterometer can measure the curing behavior of resin in molds.¹¹⁻¹³

The object of this paper is to examine the effect of hydroxides of alkali metals and alkaline earth metals on the curing behavior of resol.

EXPERIMENTAL

Resol Preparation

Phenol 940 g (10 mol), 37% formaline 973 g (12 mol), and 2.7*N* sodium hydroxide solution (74 mL) were charged in a 3-L three-necked flask fitted with stirrer, thermometer, and reflux condenser. The mixture was brought to reflux in 40 min, then held at reflux for 2 h, cooled, and neutralized with dil. hydrochloric acid, which was equivalent to the amount of sodium hydroxide added. The mixture was dehydrated under 30 mm Hg until the temperature of the mixture reached 80°C; then resol was obtained. The amount of free phenol in the resol was 10.2% (by GLC), and the consumption of formaldehyde was about 95% (the hydroxylamine hydrochloride method). Then, methyl alcohol was added to the resol to prepare a varnish with 80% resin content. Gel permeation chromatograph of the resol is shown in Figure 1.

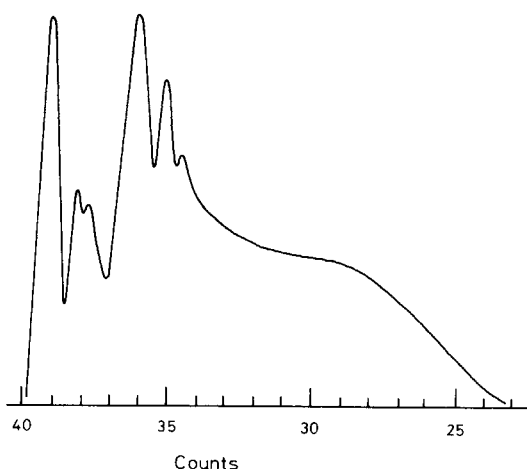


Fig. 1. GPC chart of the resol.

Preparation of the Sample for Curelastometry

Basic cure catalysts used were: LiOH, NaOH, KOH, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. The amounts of catalysts added were from 0.01 to 0.4 mol based on 100 g of solid content of resol.

The viscosity of resol is fairly low at cure temperature, and it often foams at this temperature. When resol foams, it is difficult to keep enough of it in the molds of Curelastometer. Therefore, filler was added to the resol to avoid foaming. In the preparatory experiments, the relation between the foaming behavior and both kinds and amount of fillers was examined. It was found that wood flour was a more suitable filler than the powders of silica, glass, and talc, because the pH value of resol was not changed as much and the foaming could be prevented by adding wood flour. Reproducible results were obtained by adding 40 g of wood flour to 125 g of the resol varnish, in which 100 g of resin was included. Therefore, the sample for Curelastometer was prepared in the following manner: wood flour 40 g, resol varnish 125 g, curing catalyst (0.01–0.4) were well mixed in a porcelain mortar, and then the mixture was dried under reduced pressure.

Measurement of Curing Behavior

Measurement of curing behavior was carried out by means of Curelastometer II (Japan Synthetic Rubber Co.). Sample (2.2g) was charged in the molds in which temperature was already adjusted to preset level from 140 to 170°C. The molds were closed, and the lower mold was oscillated 3 rpm at $\pm 0.5^\circ$. When the viscosity of the sample in the molds increased to a certain value during cure, the value was detected as torque by a load cell that was attached to the upper mold. Then, curing behavior of the sample, namely, the mode of increasing viscosity of the sample was obtained as a torque–time curve (Fig. 2). In Figure 2, three characteristic points are located on the torque–time curve: t_1 is the point at which the increase of torque is recognized on the chart, t_2 is the beginning of rapid increase of torque, and t_3 is a point at which the torque reaches 90% of the maximum torque. In this paper, the points are used to evaluate the cure behavior of sample, because these three points correspond to gel time, beginning time

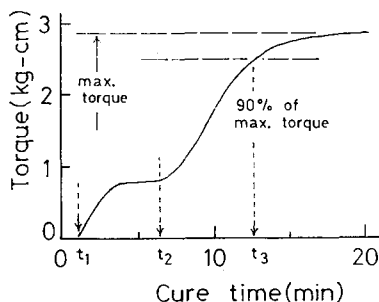


Fig. 2. Torque–cure time curve of resol (cure catalyst: NaOH) obtained by Curelastometer at 150°C.

of cure, and cure time in practical molding.^{12,13} Each plot of t_1 , t_2 , and t_3 in the following figures is the average value obtained from more than five measurements.

RESULTS AND DISCUSSIONS

Effect of Catalysts on Cure Acceleration of Resol

Curing behavior of samples containing from 0.01 mol of alkali metal hydroxides or 0.005 mol of alkaline earth metal hydroxides in resol, which had solid content of 100 g, was measured in the temperature range from 140 to 170°C by Curelastometer.

The values of t_1 , t_2 , and t_3 were obtained from torque-time curves of each sample. The co-logarithms of t_1 , t_2 , and t_3 were related to the reciprocals of absolute temperature of cure (Figs. 3 and 4). In Figure 3, curing behavior of the sample without cure catalyst is also shown (\square). Comparing each line in the figures, we find that all catalysts accelerated the curing.

The lines for t_2 and t_3 were comparatively parallel. The cure acceleration effect of catalysts both on t_2 and t_3 was estimated in the following order over the range of cure temperature: in alkali metal hydroxide, $\text{KOH} \approx \text{NaOH} > \text{LiOH}$; in alkaline earth metal hydroxide, $\text{Ba}(\text{OH})_2 > \text{Sr}(\text{OH})_2 > \text{Ca}(\text{OH})_2 > \text{Mg}(\text{OH})_2$; and in both hydroxides, $\text{Ba}(\text{OH})_2 > \text{KOH} \approx \text{NaOH}$. On the other hand, each line was not parallel in behavior with t_1 , so that the order of the acceleration effect of the catalysts could not be estimated.

Hence, the cure acceleration effect of the catalysts on t_2 and t_3 depends on the ion radius of catalysts. To verify this point, the reciprocals of t_2 and t_3 were plotted against the ion radius of catalysts.¹⁴ The relation between the cure behavior and the ion radius at 160°C is plotted in Figure 5.

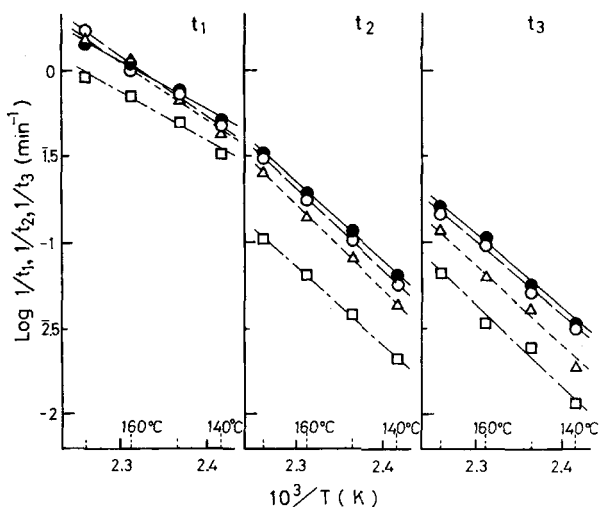


Fig. 3. Arrhenius plot for gelling and curing speed of resols with alkali metal hydroxides: (Δ) LiOH; (\circ) NaOH; (\bullet) KOH; (\square) neutralized resol.

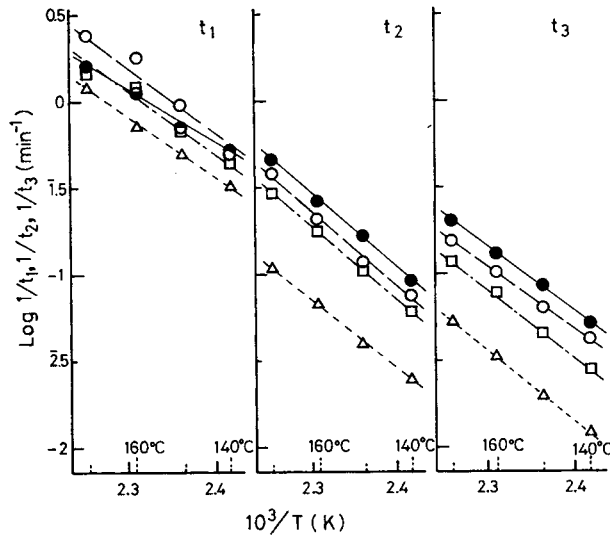


Fig. 4. Arrhenius plot for gelling and curing speed of resols with alkaline earth metal hydroxides: (Δ) $Mg(OH)_2$; (\square) $Ca(OH)_2$; (\circ) $Sr(OH)_2$; (\bullet) $Ba(OH)_2$.

Figure 5 shows that in alkali metal hydroxides, although there is not a remarkable difference in the effect of cure acceleration between sodium hydroxide and potassium hydroxide, the effects are greater than that of lithium hydroxide. In alkaline earth metal hydroxides, the effect of the catalyst on cure acceleration increases linearly with the increase in the ion radius of the catalyst.

The larger ion radius of the alkaline earth metal hydroxide resulted in a faster cure speed for the resol.

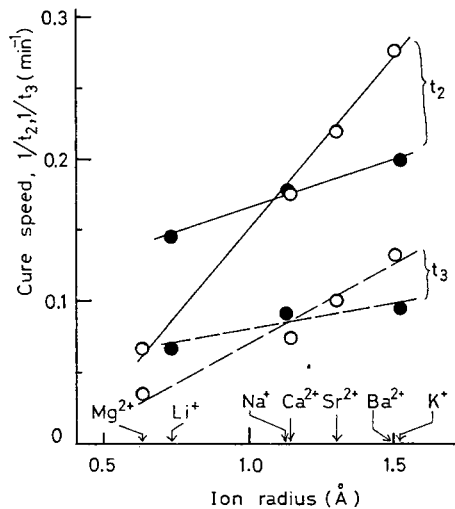


Fig. 5. Relation between cure speed of resols added with various cure catalysts and their ion radius at 160°C: (\bullet) alkali metal hydroxides; (\circ) alkaline earth metal hydroxides.

To know the temperature dependence of the gel and the cure speeds of samples containing various cure catalysts, respectively, the apparent activation energies of gel and cure speed ($1/t_1$, $1/t_2$, and $1/t_3$) of each sample were calculated from the lines in Figures 3 and 4 according to Arrhenous equation. The results are shown in Table I. Though, activation energies of gelling and curing somehow deviate, the values resembled each other in t_2 and t_3 . Temperature dependence of curing speed of resols is not changed remarkably by the addition of alkali metal and alkaline earth metal hydroxides.

Effect of Catalysts on the Acceleration of Curing

Sodium hydroxide and barium hydroxide were chosen as alkali metal and alkaline earth metal hydroxides catalysts. The effect of the amount of the catalyst added on the curing behavior of the resol was examined. Curing behavior of the samples, which contained from 0.1 to 0.4 mol of sodium hydroxide or from 0.05 to 0.2 mol of barium hydroxide, respectively, for 100 g of solid component of resol, was measured by Curelasterometer at the temperature from 110 to 150°C. The results are shown in Figure 6.

As was expected, curing speed of the samples increased with an increase in the amount of catalysts. When comparing the effect of cure acceleration of both catalysts, barium hydroxide was superior to sodium hydroxide, especially in t_1 . The dependence of the amount of barium hydroxide added on the effect of cure acceleration was also larger than that of sodium hydroxide.

Effect of Alkali Metal Hydroxides and Alkaline Earth Metal Hydroxides on Curing Behavior of Resol

The following results were obtained in this study: (i) either alkali metal or alkaline earth metal hydroxides accelerated curing speed of resol; (ii) curing speed of resol increased with an increase in the amount of the catalyst added; the dependence of the amount of catalyst on the cure acceleration was similar with both sodium hydroxide (alkali metal hydroxide) and barium hydroxide (alkaline earth metal hydroxide); (iii) the effect of

TABLE I
Apparent Activation Energy of Curing Behavior of Resols Containing Various Catalysts

Catalyst added	t_1 (kcal/mol)	t_2 (kcal/mol)	t_3 (kcal/mol)
—	12.2	19.8	21.3
LiOH	14.8	21.3	21.3
NaOH	12.6	21.1	19.8
KOH	13.0	20.5	20.0
Ba(OH) ₂	13.7	19.6	18.3
Sr(OH) ₂	17.4	19.0	17.0
Ca(OH) ₂	14.9	19.0	17.4
Mg(OH) ₂	15.3	17.9	17.9

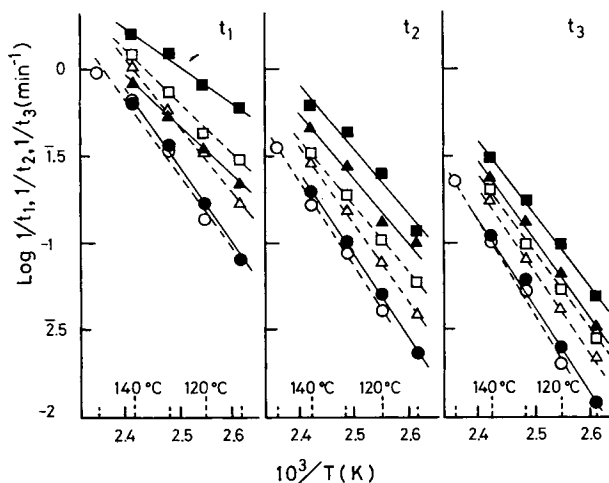
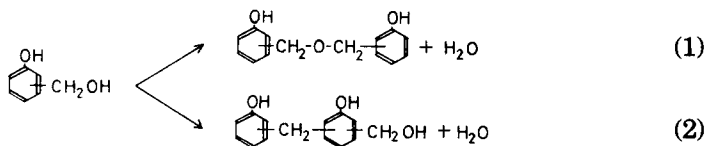


Fig. 6. Effect of the amount of cure catalysts [NaOH and Ba(OH)₂] on the curing behavior of resols: NaOH: (○) 0.1 mol; (△) 0.2 mol; (□) 0.4 mol; Ba(OH)₂: (●) 0.05 mol; (▲) 0.1 mol; (■) 0.2 mol.

cure acceleration of catalysts was in the following order, Ba(OH)₂ > KOH ≃ NaOH; (iv) in alkaline earth metal hydroxides, the effect of cure acceleration of hydroxides increased with increasing ion radius.

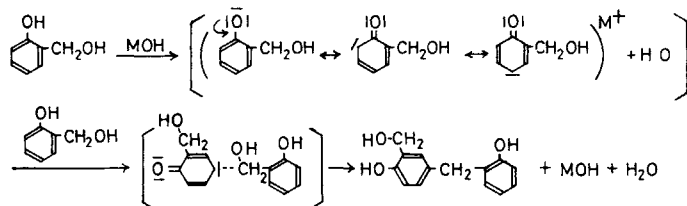
In the curing process of resol, methylol phenols react as follows:



Reaction (1) takes place in the case of high concentration of methylol group per phenolic nucleus and in neutral condition. Reaction (2) occurs in the case of basic or acidic condition. In this experimental condition, it is conceivable that curing reaction proceeds mainly according to reaction (2), because the concentration of methylol group is not so high and the condition of the resols are basic. Therefore, there is a need to discuss the relation between the behavior of cure catalysts on reaction (2) and the results described above.

Phenol reacts with sodium hydroxide or potassium hydroxide to form phenolate respectively, which dissociates to phenolate anion. The reactivity of *o*- and *p*-sites on phenolic nucleus to electrophilic reagent increases with an increase in the electron density of those sites due to the effect of electron resonance. Methylol phenols also change to their phenolate anions with basic catalysts such as alkali metal or alkaline earth metal hydroxides, and the electron density of *o*- and *p*-sites on their phenolic nuclei increases. Therefore, the reactivity of the unsubstituted *o*- and *p*-positions to methylol

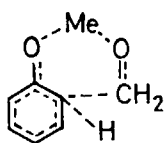
group increases with an increase in electron density of these positions as the equation shows below:



The reason for the results of (i) and (ii) described above is as follows: the effect of the catalysts on cure acceleration is due to the formation of phenolate anion of methylol phenol by addition of strong basic catalysts which dissociate highly and the increase of the concentration of them by an increase in the amount of the catalyst.

However, the result of (iii) can't be explained by the same reason on the basis of eq. (3), since basicity of barium hydroxide is smaller than that of either potassium hydroxide or sodium hydroxide. The effect of alkaline earth metal hydroxides on cure acceleration of resol is different from cases (i) and (ii).

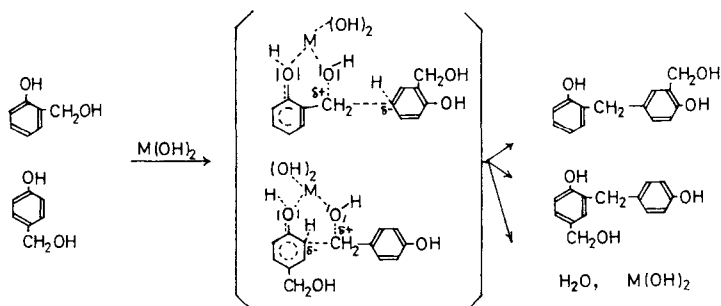
Peer³ found that, in the reaction between phenol and formaldehyde, the ratio of *o*-/*p*- of methylol phenols increased when hydroxides were used in the following sequence: K < Na < Li < Ba < Sr < Ca < Mg. To explain the result, Peer has proposed most plausible assumption by quoting from the paper by Fraser et al.¹⁵ in which reaction between *o*- sites on phenolic nucleus and formaldehyde is accelerated through the chelate formation in the transition state:



The reaction, namely, the amount of *o*-methylol phenols increases with an increase in the stability of the chelate. The stability of the chelate can be evaluated by a stability constant of chelate which is formed with metal hydroxide and ethylenediaminetetra-acetic acid. That is, the larger the value of the stability constant, the more stable the chelate. Since the value of the stability constant with sodium hydroxide was as small as 1.7, the chelate was slightly formed. In the case of potassium hydroxide, the chelate was not formed, because the value of the stability constant was too small to measure. On the other hand, as expected from the high concentration of *o*-methylol phenols in the reaction product, the stability constant of

chelate(ethylenediaminetetra-acetic acid and barium hydroxide) was as large as 7.8.

Therefore, the effect of barium hydroxide on cure acceleration of resol is due to the coordination of barium ion to methylol phenols, as illustrated below:



Barium hydroxide acts at first on the phenolic hydroxy group to enhance the electron density of *o*- and *p*-sites on the phenolic nucleus. And then, the electron density of the carbon atom in the methylol group is decreased by the chelation of barium ion to oxygen atom of the methylol group, so that electrophilic reactivity of the methylene to *o*- and *p*-sites on phenolic nucleus increases. Therefore, the effect of barium hydroxide on cure acceleration of resol involves: (a) an increase in electron density of *o*- and *p*-sites on phenolic nucleus, and (b) an increase in electrophilic reactivity of the carbon atom in the methylol group by chelate formation between barium ion and oxygen atoms in phenol and alcohol hydroxyl groups.

The action of alkaline earth metal hydroxides on the result (iv) can be described as follows. Water solubility¹⁶ of alkaline earth metal hydroxide increases with an increase in their ion radius: $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, 0.275 g-formula-weight per 1000 g H_2O at 25°C; $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, 0.0656 at 20°C; $\text{Ca}(\text{OH})_2$, 0.0218 at 20°C. And also basicity of alkaline earth metal hydroxides increases with an increase in their water solubility. We propose that the reason for the effect of alkaline earth metal hydroxide, especially barium hydroxide, on cure acceleration of resol was due to the increase in reactivity of *o*- and *p*-sites on phenolic nucleus and the increase in electrophilic reactivity of methylene linkage by chelate formation. The effect of the increase in basicity of alkaline earth metal hydroxides with an increase in their ion radius on cure acceleration of resol is greater than that of chelate formation.

CONCLUSION

Both alkali metal hydroxides and alkaline earth metal hydroxides accelerated the curing of resol, and the cure acceleration effect of barium hydroxide was the largest.

In the relation between the kinds of catalysts and the cure acceleration effect, it was found that the larger the ion radius of catalyst, the faster the cure speed of resol.

Apparent activation energies of curing behavior of the resols that contained the cure catalysts were in the range of 17.0–21.3 kcal/mol, and the values were not changed on a large scale by the difference in the kinds of catalysts.

The difference of curing behavior between alkali metal and alkaline earth metal hydroxides was also discussed.

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Received September 9, 1984

Accepted February 14, 1985