

Curing Behavior of Two-Step Phenolics by Solvent Extraction

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Synopsis

In examining the degree of cure of the novolac-hexamine system, higher-boiling polar solvents such as methylcellosolve and cyclohexanone were found to have better extraction power than that of acetone, even for resins with a relatively high degree of cure. Making use of the difference in their extraction power, the cured resins could be fractionated into four portions, i.e., acetone soluble, acetone insoluble but methylcellosolve soluble, methylcellosolve insoluble but cyclohexanone soluble, and cyclohexanone insoluble. The formation and subsequent diminution of the soluble intermediates and the increase of insoluble crosslinked resins in the curing process were shown clearly by plotting the amount of each fraction against curing time at various temperatures. Further, the same extraction procedure was applied to the resins cured under reduced pressure. The curing reaction was markedly delayed in the latter case. Based on the remarkable difference in the curing behavior under pressure, a curing mechanism has been proposed in which the moisture contained may accelerate the decomposition of hexamine, thus enhancing the reactivity of the resin system.

INTRODUCTION

Two-step phenolics are widely used in many applications, such as electrical insulators, mechanical parts, shell mold, and abrasive wheel binders, etc. This is because they exhibit excellent performance in compliance with the requirements of each application field. The performance, however, is much influenced by curing conditions, especially by the degree of cure. It is very important, therefore, to examine the curing characteristics of the resins in deciding the optimum conditions.

Many testing methods for evaluating the curing characteristics have been proposed and used in practice, for instance, acetone extraction,^{1,2} measurement of hardness at elevated temperatures,³⁻⁶ measurement of electrical resistance,⁷ IR spectrophotometry,⁸⁻¹⁰ and differential scanning calorimetry.¹¹⁻¹³

Among them, the acetone extraction method is the only chemical procedure in dealing with resin molecules that change their size in the curing process. It has been used very often, therefore, as a reference for judging the degree of cure when other physical methods are adopted. However, acetone used in the test has insufficient extraction power due to its low boiling point, thus lowering its sensitivity in examining those resins with fairly advanced cure. On the other hand, when the extraction is performed at a higher temperature with a solvent having a higher boiling point and better extraction power, higher sensitivity would be expected over a wide range up to an advanced degree of cure.

In this paper, methylcellosolve and cyclohexanone were selected as high-boiling solvents, and the extraction was performed on two-step phenolics in order to compare the results with those of the acetone extraction test. In addition, an attempt was made to fractionate some intermediates in the resins cured under

various conditions, including reduced pressure, making use of the difference in their extraction power of these three solvents.

EXPERIMENTAL

Preparation of Molding Compound

The following novolac resin was mixed with 10 phr hexamine as a curing agent, and the mixture was ball-milled. In this compound the addition of filler and lubricant was omitted so that the results could be interpreted with less complication.

The novolac resin was manufactured by Lignite Co. (trade name Sandbond C) using oxalic and hydrochloric acids as catalyst; melting point 98°–108°C (softening point 81°C); $M_n = 500$ containing about 7% free phenol; *o/p* ratio = 45/55.

The moisture content of the compound, measured by Karl Fischer aquametry in accordance with our previous paper,¹⁴ was 1.3%, which was adjusted to correspond to that of usual commercial compounds available in Japan.

Curing Conditions

Curing Under Pressure. The compound mentioned above was cured under a pressure higher than 50 kg/cm² at a temperature between 130° and 170°C using a pair of heating platens and a simple mold frame, after being tabletted (23 g, 40 mm ϕ) and rapidly preheated near the softening point by a HF-preheater (Fuji Electronic Industrial Co., roller electrode type; 80 MHz, 5 kW). The simple mold frame used was a brass plate of 150 × 150 × 2 mm with 100 mm ϕ hole in the center, which was inserted between the platens of a press to function as a mold during curing. The advantages of such a simple mold were easy controlling of curing conditions and easy removal of moldings. The moldings thus obtained were pulverized after lathing, and the powder was used as the sample for extraction.

Curing Under Reduced Pressure. About 3 g of the compound was wrapped with Al foil to a 2-mm thickness and was cured at a temperature between 130° and 160°C in a heated oil bath which was kept in a vacuum container (50–100 mm Hg). The compound was carefully kept free from heating oil contamination. At the top of the foil wrapping an opening was provided so that the gases evolved from the compound could easily escape.

Solvent Extraction of Cured Resins

After being vacuum dried at 50°C to constant weight, the cured and pulverized resin was solvent extracted using a Soxhlet extractor. Thus, the amount of resin extracted was determined and extraction percentage was plotted against curing time.

When methylcellosolve or cyclohexanone was used as solvent, a successive acetone extraction was necessary in order to effectively remove the higher-boiling solvent from the extraction residue. Furthermore, in the case of methylcellosolve extraction, it was found effective to mix 300 phr silica powder (100–150 mesh) with the resin so as to prevent troublesome blocking due to swelling.

Determination of Hexamine Remaining in Cured Resins

The amount of hexamine in the resins cured under various conditions was determined by IR spectrophotometry using KBr tablets. The ratio of optical density in the absorption band at 1010 cm^{-1} against that at 1610 cm^{-1} was measured. The former band corresponds to the C-N linkage in a hexamine molecule, and the latter is due to the double bonds of a benzene ring.

RESULTS AND DISCUSSION

Conditions for Solvent Extraction

As previously mentioned, woodflour as filler was not used in the preparation of the molding compound in order to eliminate any possible error which might arise from the simultaneous extraction of natural resins or other materials contained in the filler. Prior to all tests, the optimum condition of extraction with each solvent was examined using the resins cured under different temperatures and time.

The results of extraction with acetone and methylcellosolve are shown in Figure 1. The saturation time in the extraction was about 20 hr with acetone and 40 hr with methylcellosolve, which could be adopted as a proper extraction time. In the case of the latter solvent, the extraction took a longer time because of a lower rate of diffusion of the solvent into the resin due to its larger molecule and higher viscosity than acetone. With cyclohexanone 40 hr was adopted as the extraction time, though the saturation time was not as long (about 30 hr) as with methylcellosolve.

The powder with particle sizes passing through 80 mesh was considered suitable for the extraction, judging from the result (Fig. 2) of an experiment with methylcellosolve and a resin cured at 150°C for 20 min.

A summary of conditions adopted for the extraction tests is shown in Table I. Here, note that in spite of the high boiling point of cyclohexanone, the temperature at which the extraction is performed is fairly low (max. 125°C) at a proper refluxing rate such as 5–8 cycles/hr. Accordingly, there exists little

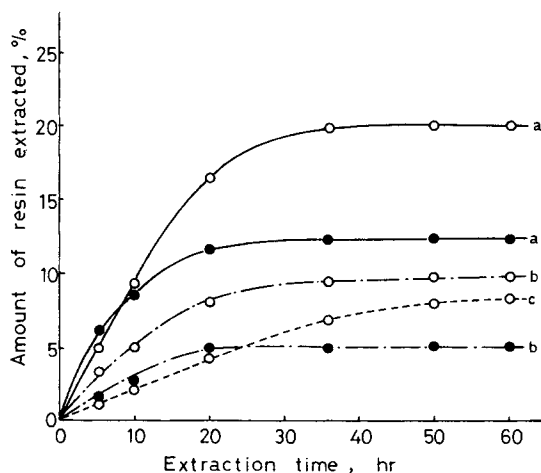


Fig. 1. Amount of extraction with time for resins cured under different conditions: (O) methylcellosolve; (●) acetone; (a) $150^{\circ}\text{C}/10\text{ min}$; (b) $150^{\circ}\text{C}/30\text{ min}$; (c) $170^{\circ}\text{C}/20\text{ min}$.

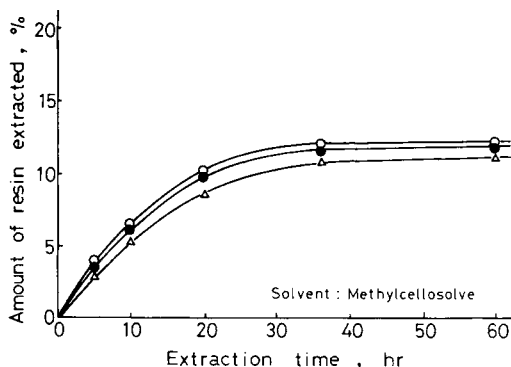


Fig. 2. Influence of particle size on extraction curve for resin cured at 150°C for 20 min. Powder size: (O) 100 mesh pass; (●) 80-100 mesh; (Δ) 60-80 mesh.

possibility of further polymerization during the extraction step which would otherwise give a significant effect to the result. Thus, all the conditions listed in the table can be used without trouble.

Fractional Extraction and Curing Behavior Under Pressure

Figure 3 shows the results of extraction tests with three different solvents on the resins which were cured from the compound containing 1.3% moisture. The extraction power of methylcellosolve and cyclohexanone, for example, against the resins cured at 150°C was roughly twice and thrice, respectively, that of acetone (Fig. 4).

Making use of the difference in the extraction power of these three solvents, the intermediates in the cured resin may be fractionated according to their molecular size and structure. Accordingly, an acetone-extractable portion was designated as Fr. 1, an acetone-unextractable but methylcellosolve-extractable portion as Fr. 2, a methylcellosolve-unextractable but cyclohexanone-extractable portion as Fr. 3, and a cyclohexanone-unextractable portion as Fr. 4. The change in the amount of each fraction with curing time was examined.

The results are shown in Figure 5. At a curing temperature of 130°C, Fr. 1 continued to decrease for the first 10 min or more; while Fr. 2 rapidly increased in the early stage (after 1 min) and soon reached the maximum (after 2 min; resin amount 50%), followed by gentle decrease. As Fr. 2 decreased, Fr. 3 began to appear and continuously increased in quantity up to more than 70% of the total resin (after 20 min), after which it was partly converted to a solvent-insoluble matter, Fr. 4. At 140°C, Fr. 3 also reached the maximum (after 10 min; 60% resin), and finally Fr. 4 attained 60% of the total.

The higher the curing temperature, i.e., 150° and 160°C, the less became the amount of Fr. 2 and Fr. 3 formed and the earlier and more the formation of Fr. 4. At 170°C, the intermediates Fr. 2 and Fr. 3 almost did not appear, with the decrease in Fr. 1 corresponding to the increase in Fr. 4. It is noticed, however, that a certain amount of Fr. 1 remained in the cured resin over the whole curing time at such a high temperature.

This evidence suggests that in the curing process of two-step phenolics, the intermediates formed react quickly with each other to grow to a solvent-insoluble matter, leaving a small quantity of small molecules. In addition, constituents in the cured resins are considerably different depending on curing temperatures.

TABLE I
Conditions for Solvent Extraction (Soxhlet Method)

Resin	Filler	Powder size	Solvents (bp)	Temp., °C	Conditions	
					Time, hr	After-treatment
Novolac-hexamine system cured under various conditions	Silica 300 phr, only for extrn. with methyl-cellosolve	80-mesh pass	acetone (56.2°C)	55	20	vacuum drying at 50°C
			methylcellosolve (124.4°C) cyclohexanone (155.7°C)	118 ± 2 120 ± 5	40 40	vacuum drying after displacing the solvent with acetone

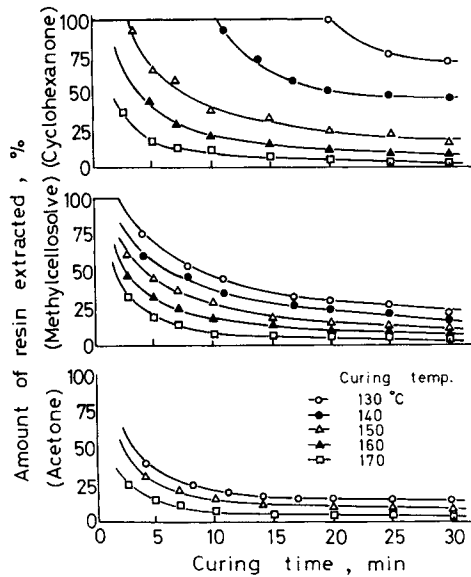


Fig. 3. Amount of extracted resin vs curing time at various temperatures.

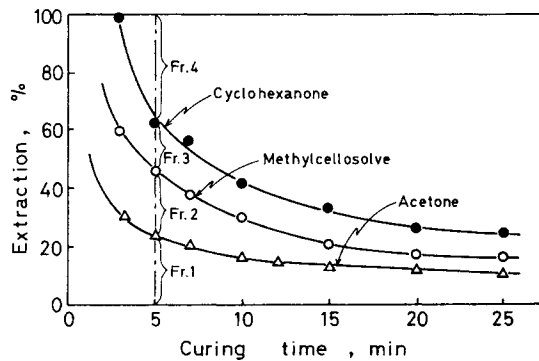


Fig. 4. Comparison of extraction power of three solvents against resins cured at 150°C.

In the resins cured at or below 160°C, there exists a considerable amount of soluble intermediates in the whole range of curing time, while in the resins cured at 170°C almost all products are insoluble due to crosslinking. This difference in the constituents of cured resins may explain a generally accepted rule of thumb that phenolic moldings change their chemical properties to some extent depending on the curing temperature above or below 170°C, because internal stresses developed in the moldings are liable to be relieved by the existence of intermediates below this critical temperature.

Curing Behavior Under Reduced Pressure

The curing behavior of the resin under reduced pressure is discussed in this section, compared to that under pressure described in the previous section. The results of the extraction tests and fractionations are shown in Figures 6 and 7, respectively.

While an acetone-insoluble matter immediately appeared after 1 min even

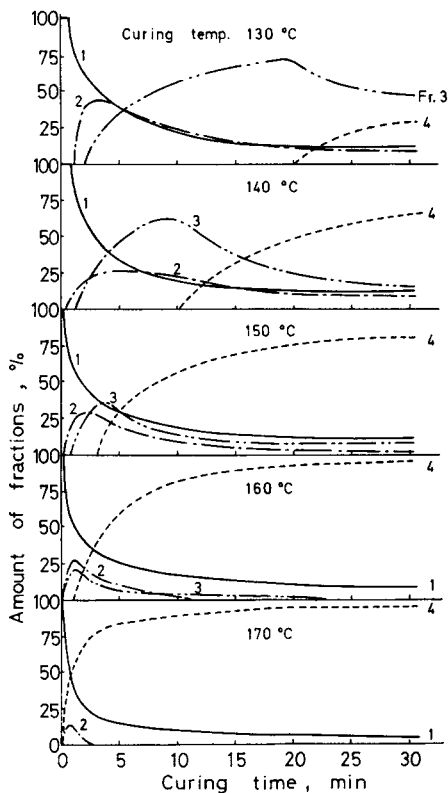


Fig. 5. Change in amount of resin fractions with curing time at various temperatures.

at the low temperature of 130°C under pressure, it was formed only after 18 min under reduced pressure. At 140°C, the pattern of formation or subsequent diminution of each fraction was very similar under high and reduced pressures, except for the difference in the rate of curing reaction. For example, under reduced pressure the progress of curing reaction was delayed by about 10 min, and the forming rate of insoluble resin was two thirds of that under pressure.

At both 150° and 160°C under pressure, the intermediates appeared in the early stage and diminished immediately, instead of which the insoluble resin rapidly formed. Under reduced pressure, however, a much greater amount of intermediates formed, and half of them remained in the cured resin system due to delaying in the succeeding reaction including crosslinking.

Effect of Moisture on Curing Behavior

There is no concrete theory on the curing behavior which largely depends upon different curing conditions such as under pressure or reduced pressure. However, the following would be a possible explanation for the difference in behavior, based on the results of experiments regarding the determination of hexamine remaining in the cured resin (Table II) and the effect of moisture on the curing behavior under normal molding conditions.¹⁵

On heating the compound containing moisture under pressure, it is likely that most of the moisture in it remains until the last moment of curing and accelerates the decomposition of the hexamine or hexamine–novolac adduct. Therefore

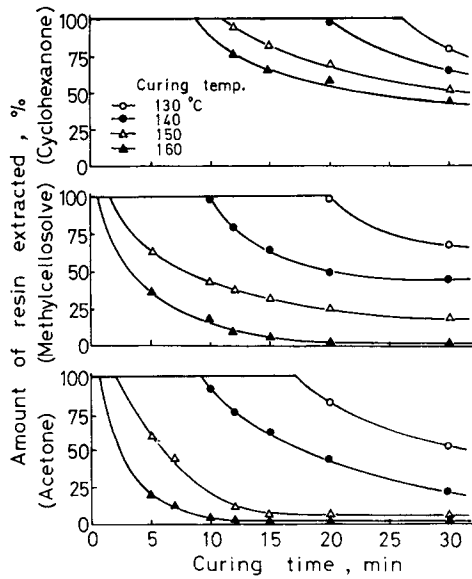


Fig. 6. Amount of extracted resin vs curing time at various temperatures under reduced pressure.

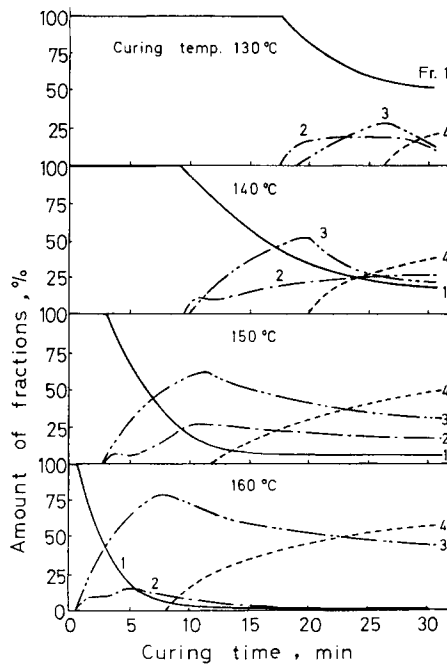


Fig. 7. Change in amount of resin fractions with curing time at various temperatures under reduced pressure.

reactive low molecular materials such as methylenimine, methylolamine, metylenediamine, or their derivatives may be formed. They immediately react with novolac to form intermediates, which are further connected with each other by the action of the above materials to produce the insoluble matter, though the curing also proceeds in parallel by the self-condensation of the intermediates.

TABLE II
Hexamine Consumption in Two-Step Phenolic Resin Cured at 150°C Under High and Reduced Pressures

Curing time, min	Residual hexamine, %	
	High pressure	Reduced pressure
Just after melting	29.3	—
3	4.2	44.7
10	3.2	38.8
30	4.6	35.7

In addition, it may be possible to partly explain this experimental fact by the action of ammonia which is generated during curing and also accelerates the decomposition of hexamine in a way similar to the moisture.¹⁶

On heating the compound under reduced pressure, on the other hand, most of the moisture (and ammonia) is removed in the early stage. Consequently, as the decomposition of hexamine is not smoothly performed, there remains a considerable amount of hexamine in the system throughout the whole curing process. Thus, the curing reaction will be delayed. At the same time, the reactive low molecular weight materials formed by the decomposition of hexamine are removed easily under such a reduced pressure. This would also be one of the causes which delayed the curing reaction.

In conclusion, moisture plays an important role in the curing of the novolac-hexamine system, in which it seems to act as a catalyst for the decomposition of hexamine. The formation of reactive low molecular weight materials, which is presumably based on the study by Richmond¹⁷ on the formation of hexamine from ammonia and formalin, may be an essential part of the curing reaction. It is necessary, of course, to identify these materials by further investigations in order to prove the authors' presumption. This important problem, however, seems to be beyond the scope of the present paper. It should be clarified in the near future.

CONCLUSIONS

The fractional extraction with a combination of solvents having different extraction power was recognized as an effective means to examine the curing behavior of two-step phenolics. It was found by this method that there was a large difference between curing behavior under pressure and that under reduced pressure, with delaying in curing reaction in the latter case. The difference presumably is caused by the accelerating effect of moisture on the decomposition of hexamine during curing.

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