

Cure Rates of Phenolic Resins by Differential Thermal Analysis

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Synopsis

A method has been developed to show the effect of temperature, catalyst level, resin advancement, and water content on the cure rate of phenolic resins by DTA. This DTA procedure allows for quantitative measurement of the phenolic resin cure exotherm.

INTRODUCTION

Differential thermal analysis is the measurement of the temperature of a sample as compared to an inert reference material when both are either heated or cooled. The sample may undergo physical or chemical changes which will result in either a heat loss (endotherm) or heat gain (exotherm) that can be measured with respect to the temperature at which the phenomenon takes place. Inorganic materials such as minerals have been studied by this method over the years, but the advent of modern electronic equipment now makes it possible to work with the more difficult organic compounds particularly polymers. Characterization thermograms have been obtained on certain polymers,^{1,2} and some quantitative results have been obtained by Johnson et al.³ on the polyester-styrene copolymer, but little quantitative work has been performed on the thermosetting phenol-formaldehyde polymer.

This paper deals with the curing rates of phenolic resins and factors which effect these rates, as determined by differential thermal analysis. A brief report was written by Ravich⁴ on the differential thermal analysis of phenol-formaldehyde resins, and a more complete investigation was performed by Nakamura,⁵ but in neither case were definite cure rates for phenolic resins determined. During the cure of a phenolic resin, an exotherm occurs between 135 and 150°C. which is attributed⁴ to a condensation reaction taking place in the resin. As the resin becomes more highly cured, the exotherm gradually diminishes in magnitude. Measurement of this cure-dependent exotherm at different times during the cure cycle gives a reliable cure rate curve of the resin from the friable state to the point where the exotherm has disappeared. To obtain these exotherm measurements many variables,⁶ such as heating rate, composition and design of the sample

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holder, sample quantity, dilution ratio with inert material, degree of packing, particle size of the sample, were controlled.

EXPERIMENTAL

DTA Apparatus

The furnace consists of a cylindrical brass block which has been drilled to contain a central cartridge heater and four Pyrex glass sample holders. Temperature programming is accomplished by the use of a motor driven autotransformer. Iron-constantan thermocouples (butt-welded B & S gauge 25) were used, and the emf output recorded on Leeds & Northrup H AZAR recorders. The apparatus is shown in Figure 1.

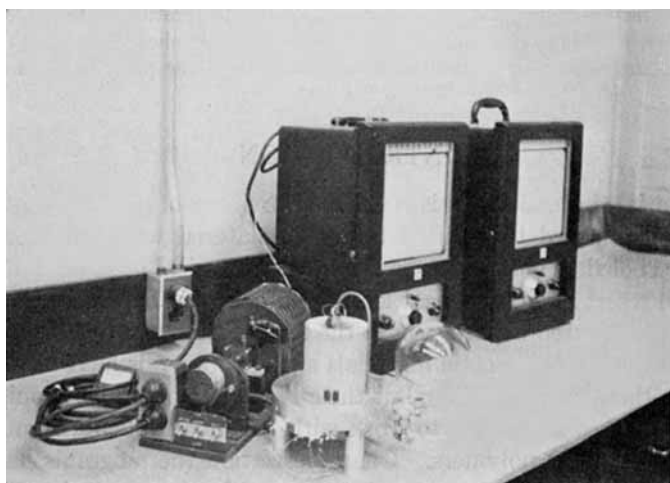


Fig. 1. DTA apparatus.

Preparation of Phenolic Resins

Five phenolic resins were prepared as shown in Table I. The reactants (phenol and paraformaldehyde) were weighed into a reaction vessel equipped with a water condenser, a stirrer, a thermometer, and a vacuum out-

TABLE I

Resin no.	Wt. reactants, g.		Para-formaldehyde	Catalyst (50% NaOH), g.	Reflux time, min.	Viscosity (25°C.), c poise	pH	H ₂ O, %
	H ₂ O	Phenol						
1	7.2	57.0	34.4	0.54	105	47,000	7.17	11.68
2	7.2	57.0	34.4	0.54	60	2,100	7.32	11.30
3	7.2	57.0	34.4	1.08	60	10,000	7.62	13.97
4	7.2	57.0	34.4	1.61	60	100,000	7.90	8.89
5	7.2	57.0	34.4	1.61	60	56,000	7.90	14.07

let. The reactants were heated to 60°C. under a slight vacuum and the catalyst (50% sodium hydroxide solution) added. The reaction mixture was then slowly heated to reflux ($100 \pm 1^\circ\text{C}.$) with stirring for 1 hr. The pH, viscosity, and water content were then determined on each resin, as described in Table I.

Resin 4 was refluxed under conditions which allowed for the removal of some water from the resin system. A portion of resin 5 was diluted with water so that a water content of 22% was obtained.

Each of the resins in Table I were drawn as films (6 mil) on aluminum foil strips and placed in a curing oven at a temperature of 93.3°C. Samples of each of the resin films were removed from the oven at definite time inter-

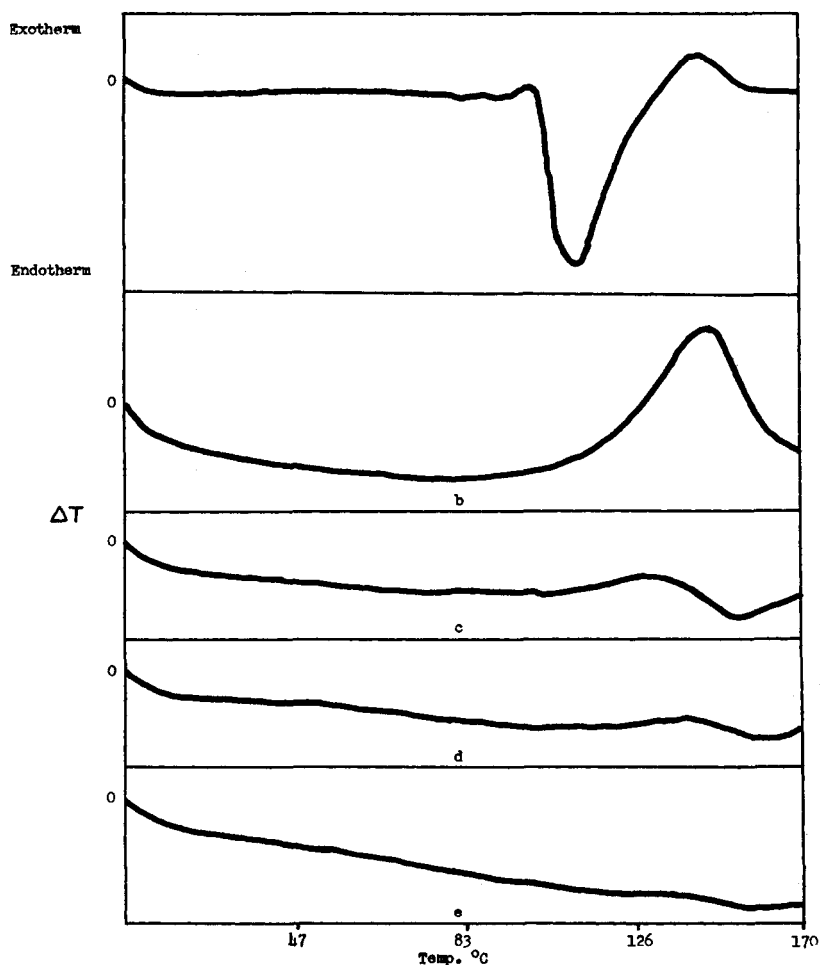


Fig. 2. Thermograms of phenol-formaldehyde resin 4, cure temperature 93.3°C., heating rate 5.6°C./min.: (a) uncured; (b) 55 min.; (c) 60 min.; (d) 100 min.; (e) 240 min.

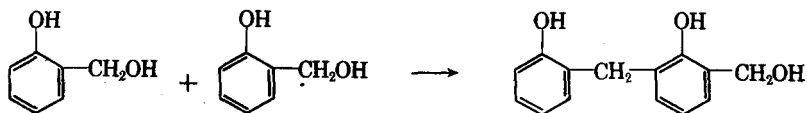
vals and quenched with Dry Ice to prevent further advancement of the resin.

DTA Procedure

The resin films were ground with Dry Ice to pass a 78 mesh screen to insure more uniform particle size. A 50-mg. sample of the ground resin was then mixed with 50 mg. of potassium bromide and pelletized onto the thermocouple by means of a die and a press. The pelletizing technique insures more accurate placement of the thermocouple in relation to the sample and also gives more intimate contact between the sample and thermocouple. (Addition of potassium bromide to the resin system made the pellet formation easier and more uniform than could be obtained with Al_2O_3 . Thermograms were run on potassium bromide pellets versus aluminum oxide reference material, and no inflections occurred in the thermogram from ambient to 250°C . which was the temperature range where the resin samples were run.) A 100-mg. pellet of potassium bromide was then pressed on the reference thermocouple. The sample and reference pellets, with the thermocouples in place, were then inserted into Pyrex glass sample holders and covered with 150 mg. of aluminum oxide powder. The Pyrex tubes were placed into the brass heating block and the furnace module assembled. The temperature of the furnace was programed at $5.6^\circ\text{C}/\text{min}$. rise from ambient to 200°C . The thermogram of the sample (time versus differential temperature) and the block temperature were recorded. Correlation of the two charts gave the final thermogram (temperature versus differential temperature). The degree of cure of each specific sample is determined by measurement of the area under the cure exotherm which appears between 135 and 150°C . Figure 2 shows a series of cure exotherms of phenolic resin 4, which was cured at 93.3°C . for varying lengths of time; as the resin cure increased, the area under the exotherm diminished.

DISCUSSION

It was assumed in this work that the area under the exothermic peak which occurred near 150°C . was a function of the heat liberated by the resin during condensation reactions such as the formation of methylene bridges from methylol groups:



Therefore, the rate of change of the area under this peak would be a measure of the degree of cure. When the peak diminished to a level where area measurements were unreliable, the resin was considered fully cured.

A one-stage commercial resol gave a hardness at this point which was equivalent to the hardness achieved in a final commercial product.

DTA thermograms were run on the resins in the liquid or uncured state, but the quantitative measurements of the exotherm areas were not repro-

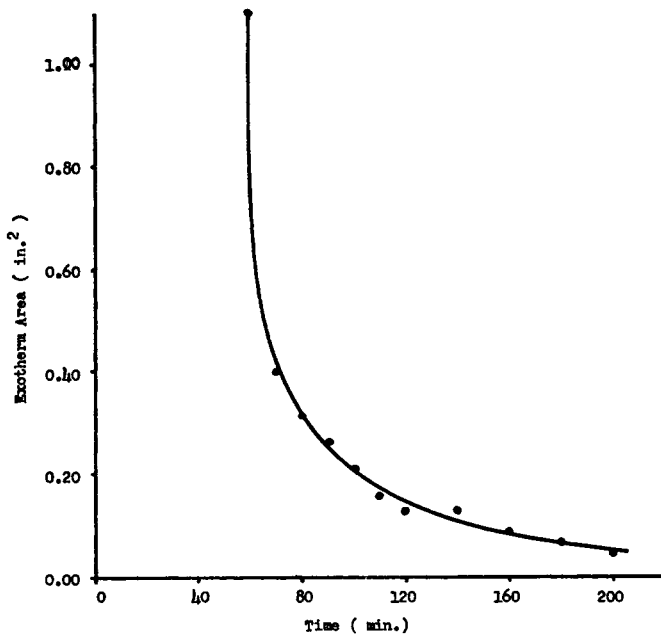


Fig. 3. Exotherm area for resin 3, cure temperature 93.3°C.

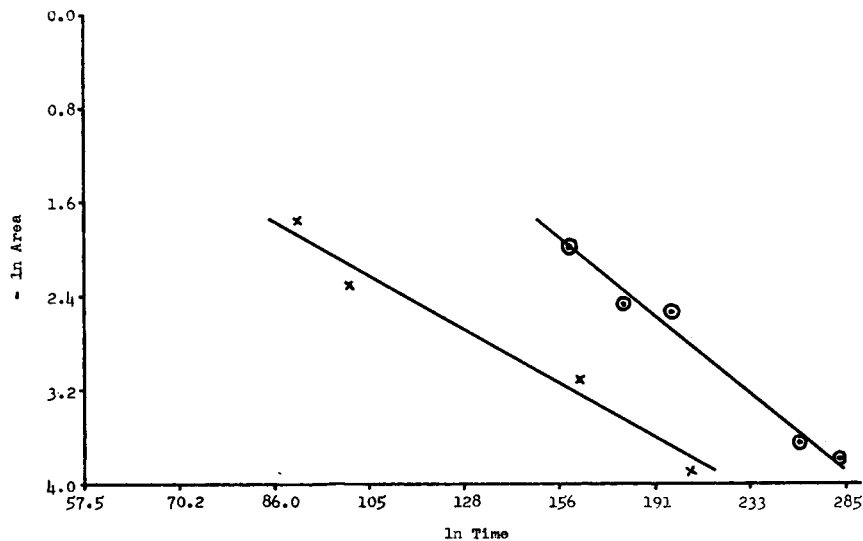


Fig. 4. Effect of reflux time on resin cure rate: (X) 105 min. reflux, resin 1; (O) 60 min. reflux, resin 2.

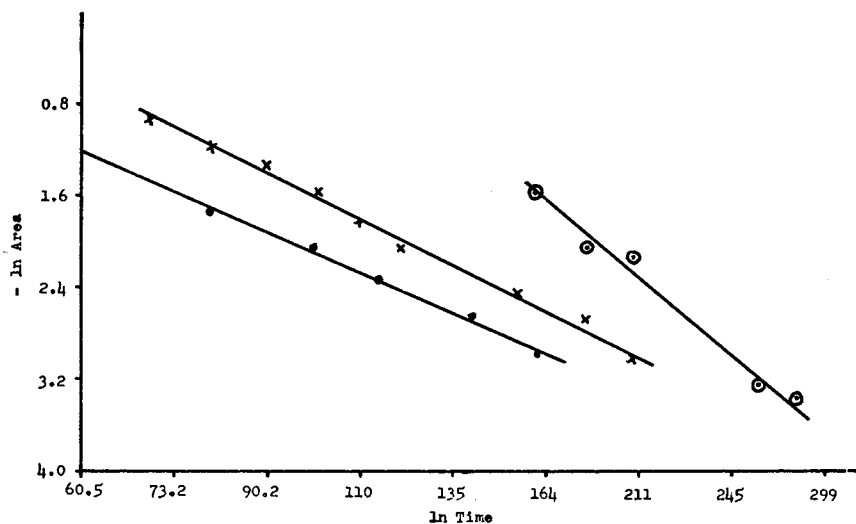


Fig. 5. Effect of catalyst on resin cure rate: (●) 0.81% NaOH, resin 5; (×) 0.54% NaOH, resin 3; (⊙) 0.27% NaOH, resin 4.

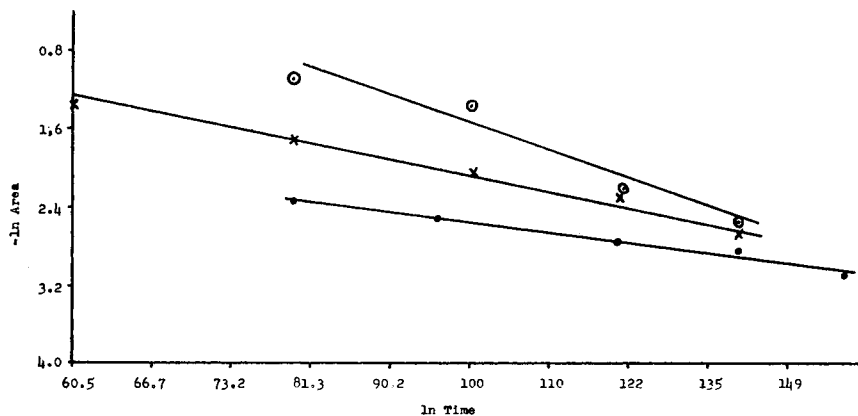


Fig. 6. Effect of water on resin cure rate: (●) 9% H₂O, resin 4; (×) 14% H₂O, resin 5; (⊙) 22% H₂O, resin 5.

ducible. The reason for this was interference of an endotherm from volatile materials just prior to and overlapping the cure exotherm and movement of the thermocouple due to volatiles boiling from the resin. It was found that reliable results were obtained after the resin had been cured to the friable state—defined as that point where the resin first becomes a brittle glassy material—and the above interferences were no longer present. The transition of the resin from the gummy state to the friable state was so rapid that reliable sampling was difficult in this range. Figure 3 gives an example of the rate of cure of the resin from a semisolid to final cure. The validity of the initial point is questionable due to the aforementioned rea-

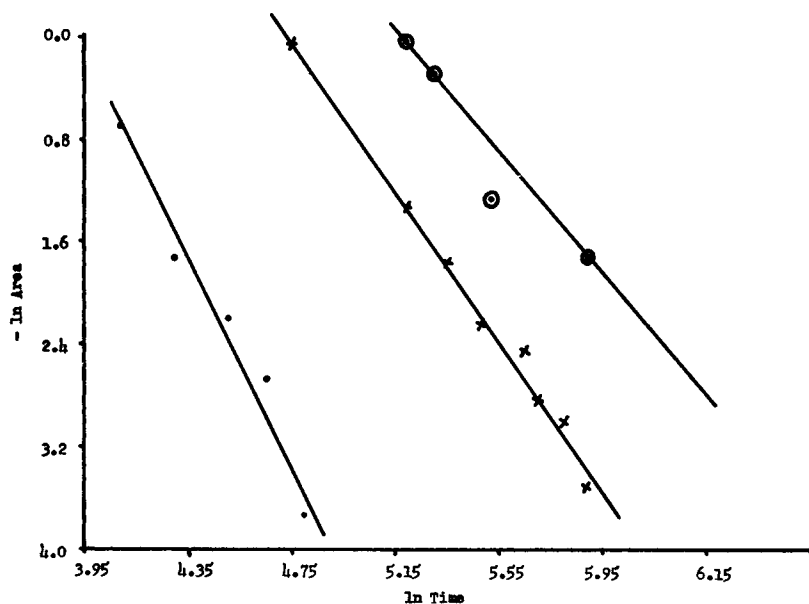


Fig. 7. Effect of temperature on resin cure rate for commercial phenolic resin: (●) 107.5°C.; (×) 93.3°C.; (⊙) 80.0°C.

sons, but the remaining points are reproducible. The rate curves for the various phenolic resins (Figs. 4-7) were drawn from the friable to the cured state. A logarithmic plot of time versus area results in a relatively straight line. The slopes of these curves were used as a measure of cure rate. The total time to cure, for each resin, was taken as the time from initiation of the cure to the time required for the cure exotherm to diminish to a point where it could no longer be measured.

Figure 4 shows the effect of reflux or cook time on cure rates (resins 1 and 2). Resin 1 (105 min. reflux) required less time for total cure. This was expected, since the resin was more advanced at the initiation of the final cure. Although resin 2 (60 min. reflux) required a longer total time to full cure, comparison of the rate from the friable to the cured state shows resin 2 has the faster rate in this region.

The effect of catalyst level (Fig. 5) indicates that less total time (liquid to fully cured state) is required for cure of higher catalyzed systems. However, the slopes from the friable to the cured state are again reversed with respect to the overall rates. The curves, as shown in Figure 5, show a faster rate for lower catalyst content. The effect of initial water on the total curing time of the resin is not appreciable, but the higher the initial water content the steeper the slope (Fig. 6).

To study the effect of temperature on cure rates, a commercially available one-stage resole was used (Fig. 7). Temperature, as would be expected, has the greatest effect on the total time required to cure. The higher the temperature, the less cure time required. It is also seen that higher

temperature increases the rate of cure from the friable to the fully cured resin. This latter effect is a reversal from that shown with catalyst, cook time, and water content.

While the effect of each of the variables on total cure time was as would have been predicted, the reversal of rates from the friable to the cured state is at present unexplained.

Further work is under way with the aim of obtaining additional information on the cure of these resins in the region prior to the friable state. Procedures must be developed to overcome the interferences described earlier.

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Résumé

On a mis au point une méthode par DTA pour montrer l'effet de la température, de la concentration du catalyseur, du degré de conversion de la résine et de la teneur en eau sur la vitesse de formation de résines phénoliques. L'analyse thermique différentielle permet des mesures quantitatives de l'évolution exothermique de la résine phénolique.

Zusammenfassung

Eine Methode zum Nachweis des Einflusses von Temperatur, Katalysatorniveau, fortschreitender Harzbildung und Wassergehalt auf die Härtungsgeschwindigkeit von Phenolharzen durch DTA wurde entwickelt. Dieses DTA-Verfahren gestattet eine quantitative Bestimmung der Phenolharzhärtungsexothermie.

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