

Thermal Analysis of Thermosetting Phenolic Compounds for Injection Molding

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Synopsis

The differential scanning calorimetry technique has been applied to investigate the curing of injection molding phenolic compounds. The data obtained include degree of cure, rate of curing, and heats and temperatures of curing as function of various heating rates, rate constants, energy of activation, and glass transition temperature. The curing temperature and heating rate were found to affect both the curing reaction kinetics and the final structure of the crosslinked network. The glass transition temperature changes continuously with the extent of curing, approaching the cure temperature.

INTRODUCTION

The recent progress in the area of thermosetting materials, namely, the development of injection molding compounds, has expanded their use and thus their production and processing. The injection molding of thermosetting materials is in certain aspects more complex than the injection molding of thermoplastics. During their path through the injection molding machine, the thermosettings undergo, in addition to rheological changes, also exothermic chemical reactions. The two simultaneous processes strongly affect each other; and, therefore, a delicate balance between material flow and heat flux has to be maintained. Because of the process complexity, prior to their molding, the thermosetting compounds have to be thoroughly characterized with respect to their behavior under shear flow and temperature programming.

Most recent reports deal with the rheological aspects of the molding process taking in consideration the time effect, namely, the chemical and structural changes taking place during the measurements. The reactivity and the exothermic nature of the thermosetting materials call for basic study of their curing reactions. The curing characteristics include the degree of cure, temperature, and duration of the curing reaction and the magnitude and variability of the heat of reaction as a function of time and temperature. These should be followed for isothermal and nonisothermal reactions. Differential scanning calorimetry (DSC) has been applied to obtain the above-mentioned information for thermosetting materials, other than phenolics, such as diallyl phthalate,¹ various epoxy resins,^{2,3} and polyesters.⁴

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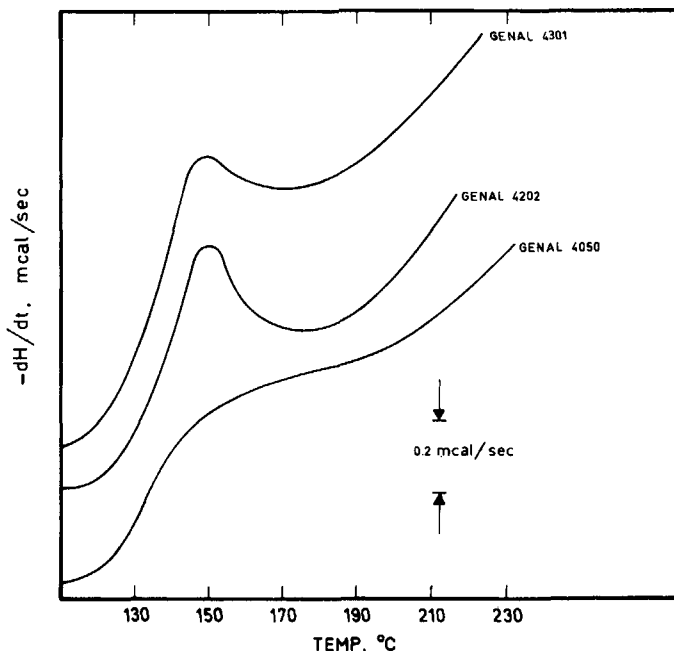


Fig. 1. DSC thermograms of three grades of Genal (heating rate of $10^\circ\text{C}/\text{min}$; the minus sign of dH/dt is to conform with the standard nomenclature for DSC, namely, negative dH/dt for "exotherm").

The purpose of the present work is the characterization of the curing reaction of injection molding phenolic compounds by the DSC technique.

EXPERIMENTAL

The injection molding phenolic compounds used in the present study were General Electric Genal 4050 (General Purpose), 4202 (Impact) and 4301 (Heat Resistant). Since these materials are commercial compounds, they are not pure phenolic resins but include also high contents of additives, mainly fillers. Thus, their composition will probably affect the experimental results. The as-received granular material was ground to powder prior to its thermal analysis.

A du Pont 990 thermal analyzer equipped with a DSC cell was employed to obtain the exothermic curing reactions data and to determine the glass transition temperature (T_g) of partially cured samples. The scanning conditions will be specified later in the text. The DSC cell was calibrated at the running conditions for temperature and heat of fusion using standard materials which melt in the temperature range of interest. The sample weight used in the DSC cell was in the range of 9 to 11 mg. Since Manley⁵ has reported the strong dependence of the area under the exothermic peak per unit weight obtained in curing various sizes of epoxy resin samples, the sample size was carefully kept in the 9- to 11-mg range.

RESULTS AND DISCUSSION

The curing of various grades of the injection molding phenolic compounds was found to be different in respect to the total heat of reaction and the temperatures

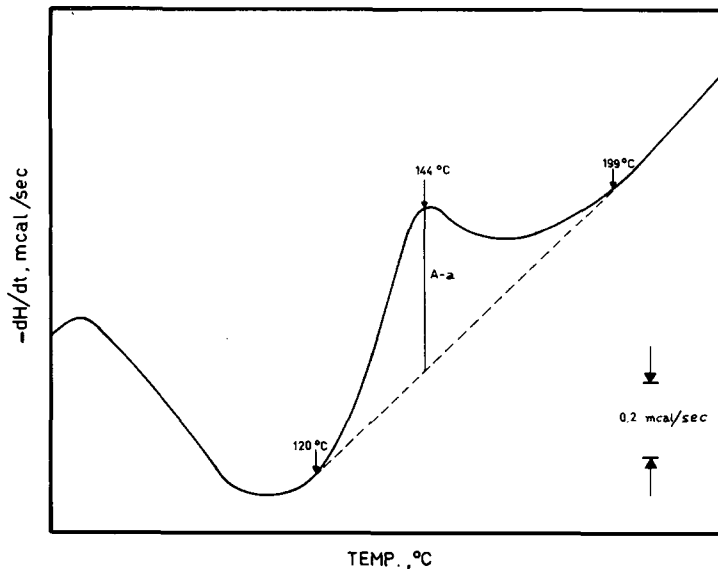


Fig. 2. Typical DSC exotherm of Genal 4050 compound (heating rate of 10°C/min).

at which the reactions were initiated, peaked, and terminated (see Fig. 1). It has been already suggested⁶ that the clear differences between thermograms of various grades enable the use of the DSC technique to characterize and differentiate between these materials. In the present work, general-purpose grade (Genal 4050) was thoroughly studied as a representative of the injection molding phenolic compounds.

An unsuccessful attempt has been made to study the curing reaction isothermally. At temperatures up to about 150°C, the curing reaction proceeds very slowly and the resulting exotherm is too slight to obtain accurate and meaningful data. At temperatures higher than 150°C, the curing rate is too high to enable recording the initial stage of the reaction. (The DSC technique requires a finite time to heat up to the desired isothermal temperature.) As a result of the described behavior, this work had to be limited to the dynamic, nonisothermal technique and isothermal data were obtained indirectly.

Figure 2 shows a typical DSC thermogram for Genal 4050 resin, using a heating rate of 10°C/min. The reaction started at 120°C (departure from the baseline), reached a maximum at 144°C, and completed (return to the baseline) at 199°C. The area under the exotherm (A) is assumed to be proportional to the heat of reaction (H^0). It is also assumed⁷ that the amount of reacted material is given by the area (a) to the left of an ordinate (dotted line) at any particular time and temperature. For first-order reactions, the reaction constant k , will be⁷

$$k = \frac{dH/dt}{A - a}$$

The reaction rate constants for a series of temperatures can be obtained from a single DSC thermogram by measuring the heights of the ordinate at given temperatures and the areas to the right of these ordinates under the curves. Kinetic data for Genal 4050 resin, as measured and calculated from Figure 2, are

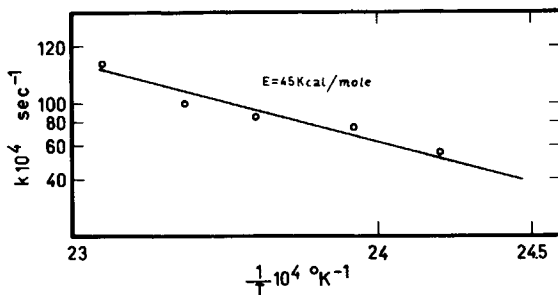


Fig. 3. Arrhenius plot for curing at a heating rate of 10°C/min of Genal 4050 compound.

given in Table I. The Arrhenius plot for these data is shown in Figure 3 over the reaction temperature range. Since the linearity of the data is good (was checked by linear regression analysis), it can be assumed that the curing reaction is indeed of first order. The calculated activation energy is 45 kcal/mole.

The Dynamic DSC method can also be employed to obtain reaction rate curves, by scanning at various rates. The Genal 4050 resin was analyzed at various heating rates in the range of 1° to 50°C/min; the thermograms are shown in Figure 4. It has been observed that the peak temperature shifts to higher value with increasing the heating rate. As shown in Table II, the peak temperature increases from 135° to 174°C in the studied range of heating rates, a shift of about 40°C. In addition, the total heat of curing was found to be dependent on the heating rate, increasing with heating rate up to a maximum followed by a decrease. This phenomenon has been observed also by Fava³ for other thermosetting materials. The shift in peak temperature, caused by the time and temperature dependence of cure and the variation in total heat of cure, may be due to a change in the cure mechanism as suggested by Fava. There is probably an optimal temperature, at which the cure mechanism is most efficient, where the heat of curing attains a maximum.

From the above-mentioned set of thermograms, it is possible to calculate and draw isothermal reaction rate curves at various temperatures.³ These temperatures are, however, limited to the temperature range common to all thermograms. The extent of cure as a function of time was calculated as the ratio of the reaction heat up to a certain temperature (H) to the total heat of reaction

TABLE I
Kinetic Data^a for Genal 4050 Compound

$T, ^\circ\text{C}$	$10^4/T, ^\circ\text{K}^{-1}$	$dH/dt, ^b$ mcal/sec	$A - a, ^c$ mcal	10^4k^d sec ⁻¹
140	24.21	0.38	69.50	55
145	23.92	0.43	57.95	74
150	23.62	0.34	40.08	85
155	23.36	0.27	28.71	94
160	23.08	0.20	17.20	116

^a Heating rate of 10°C/min.

^b dH/dt = Rate of heat evolution.

^c A = Total area under DSC exotherm; a = area under DSC exotherm to time t .

^d k = First-order reaction rate constant.

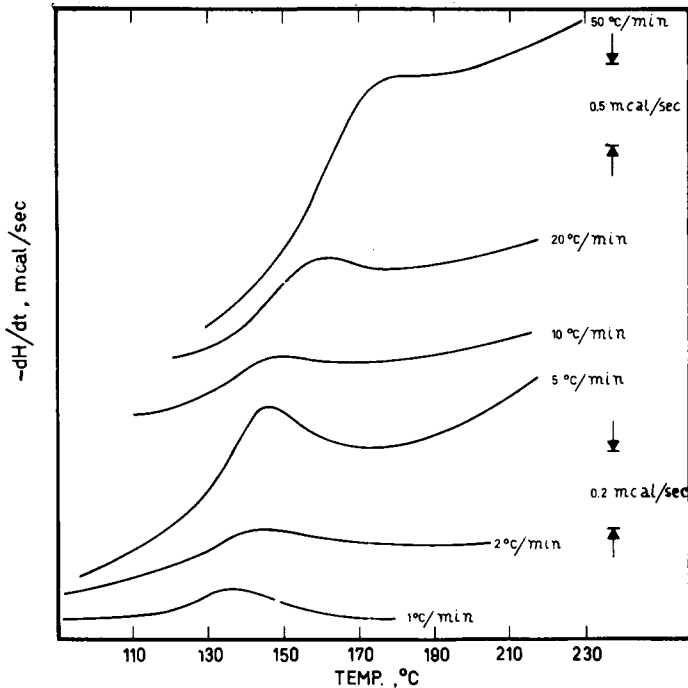


Fig. 4. DSC thermograms of Genal 4050 compound, obtained at various heating rates.

(H^0). The rate curves obtained (see Fig. 5) have a typical "S" shape. At higher isothermal cure temperatures, the initial parts of the curves are steeper, and after leveling off, they approach faster completion.

The effect of heating rate, as shown above, is very significant and thus important for the processors of thermosetting materials. As mentioned in the introduction, the main problem in processing these materials is to keep a delicate heat balance which affects both the rheology and the curing process. The heating rate of these materials during their processing is controlled by the heat supplied externally, the heat formed due to internal friction, and the exothermic curing reaction, which mutually affect each other.

The DSC dynamic method can be also employed to estimate the degree of cure by measuring the residual heat of reaction, namely, the heat evolved during the curing of the residual uncured component of the material.

TABLE II
Dynamic DSC Data of Genal 4050 Compound at Various Heating Rates

Heating rate, °C/min	Heat of reaction, mcal/mg	Exotherm peak temperature, °C
1	7.1	135
2	8.1	140
5	11.3	142
10	7.6	146
20	6.7	156
50	8.1	174

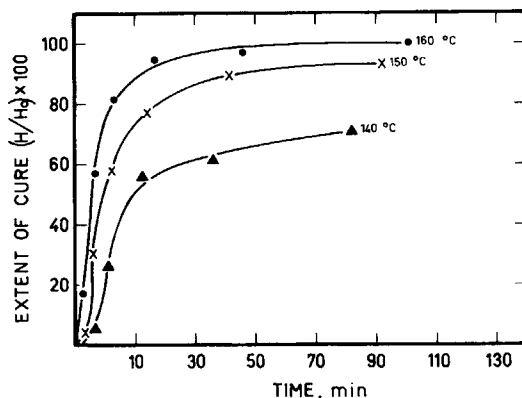


Fig. 5. Rate curves of Genal 4050 compound cured at various temperatures.

This method was used to study the effect of processing in an injection molding machine on curing of thermosetting phenolic compounds as follows: One set of samples was prepared by isothermal curing in the DSC cell for 15 min at three temperatures (180°, 190°, 220°C). Another set of samples was prepared by injection molding the material into a mold at three temperatures (170°, 190°, 210°C). The temperatures in the machine were 65°C in the feeding zone, 110°C in the cylinder, and 100°C in the die. All samples were thermally analyzed at the same heating rate of 20°C/min, and their degrees of cure were calculated from the measured residual heats of reaction. As can be seen in Table III, the injection-molded samples reached higher degrees of cure; this inspite their much shorter residence time at the given temperature (in the order of seconds). The higher degree of cure in the molded samples compared to the isothermally cured samples is a result of the precuring process taking place in the machine.

Second-order transitions of crosslinked networks have been investigated by Gordon⁸ and Fava,³ and the temperature of the transition was shown to increase with the extent of cure. It has been suggested^{3,5,9} that for resins that show a glass transition, the T_g provides an index of degree of cure. This might be useful in analyzing samples with high degree of cure, thus showing a small residual exotherm. Barton reports⁹ that during the final stages of the curing reaction of an epoxy resin, there is a large increase in T_g where measurements of the residual heats of reaction are least sensitive.

Genal 4050 samples were cured isothermally at two temperatures, 170° and

TABLE III
Degree of Cure as a Function of Curing Conditions

Isothermally cured		Injection molded	
Curing temperature, ^a °C	Degree of cure, ^b %	Mold temperature, ^c °C	Degree of cure, ^b %
180	74	170	90
190	88	190	97
200	100	210	100

^a Cured for 15 min in the DSC cell.

^b Determined at heating of 20°C/min.

^c Residence time in mold was 8 sec.

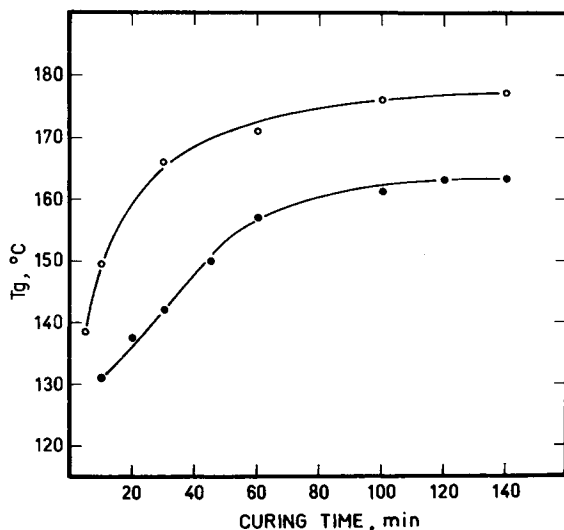


Fig. 6. T_g of Genal compound after curing at 170°C (●) and 180°C (○).

180°C, in the DSC cell for various desired lengths of time up to 140 min. Following cooling of these samples to ambient temperature, their T_g was determined at a heating rate of 20°C/min. T_g was defined as the point of intersection of the extrapolated baseline at the low temperature end and the tangent to the curve at the inflection point. The T_g was found to increase with extent of cure, approaching a limiting value which is lower than the cure temperature in agreement with Fava's results on epoxy resins.³ As can be seen in Figure 6, there is a change of about 35°C in the T_g of samples cured at the studied temperatures.

The change in T_g for phenolic compounds is not as large as for the epoxies mentioned above.^{5,9} Most of the change in the T_g of Genal takes place during the first 60 min of the curing reaction and then levels off where the degree of cure did not reach yet very high values. For example, after 60 min at 180°C, the measured degree of cure was only 75% and the corresponding T_g was already 171°C. It is important to mention that the T_g determination of highly cured compounds is inaccurate as a result of the thermogram geometry in the T_g range.

It is interesting to note that the T_g -versus-curing time curves (Fig. 6) are almost parallel in their upper part. This means that the T_g of highly cured samples cured at 170°C is always lower than that of highly cured samples cured at 180°C. It is also important to note that the T_g never exceeds the cure temperature. Hence, the final three-dimensional structure of the crosslinked material depends on the curing temperature. Curing at the lower temperature results in a structure enabling more segmental motion than in samples cured at the higher temperature. The curing temperature, at least for this particular material, affects not only the rate of curing, but in addition it affects the structure of the final product and hence it should affect its properties.

Since all samples used for studying the effect of curing on T_g were only partially cured, each of their thermograms included also an exothermic peak resulting from the completion of the residual curing. It has been observed that with increasing the initial degree of cure (larger initial curing time) the exotherms and thus the curing reactions shift to high temperatures, which are always above

T_g , and the area under these exotherms has decreased. In addition, as the T_g of the partially cured resin increases, it approaches the residual cure temperature but never exceeds it. As T_g and cure temperature get closer, the cure reaction kinetics and the final structure become probably dependent on processes controlled by segmental motion. As has been observed in the case of an epoxy resin,³ the curing reaction is very limited at temperatures under T_g ; hence, the glassy state provides a large barrier to the curing reaction. This should lead to the conclusion that curing should be carried above the resin-limiting T_g to obtain better physical properties.

In the present work, it has been shown that DSC is a very powerful technique for the characterization of various injection molding phenolic compounds. The dynamic DSC method has been employed to obtain kinetic data and reaction rate constants. It was found that the curing reaction, in the range studied, obeys first-order kinetics. The results indicate an optimal temperature, at which the cure mechanism is most efficient, where the heat of curing attains a maximum.

The T_g was found to be closely related to the extent of cure, increasing with the latter and approaching a limiting value characterized by the cure temperature. Since the curing reaction is very limited at temperatures under T_g , curing should be carried above the resin-limiting T_g to obtain better physical properties.

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