

Heats of Reaction and Kinetics of a Thermoset Polyester

S. Y. PUSATCIOGLU,* A. L. FRICKE,† and J. C. HASSLER,‡ *Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia*

Synopsis

The curing reaction of a thermoset polyester was investigated by using the isothermal and dynamic techniques of differential scanning calorimetry (DSC). The heats of reaction (at different curing temperatures) and a kinetic expression of the crosslinking reaction are presented and compared to the results of the previous studies. The proposed kinetic model can be utilized to obtain the rates of heat generation and the extent of cure at different cure temperatures and time. The overall activation energy of the curing reaction was calculated on the basis of experimental data as 17.0 kcal/mole and the overall reaction rate constant as $2.60 \times 10^9 \exp(-17,000/RT) \text{ min}^{-1}$.

INTRODUCTION

The physical, mechanical, and electrical properties of a thermosetting material depend upon the extent of the polymerization reaction during cure or upon the degree of cure in the molded material. Determining such dependence is not only important for a better understanding of structure–property relationships, but it is also fundamental in optimizing the properties of the final product.

The crosslinking reaction of thermosets is a highly exothermic process, and heat thus liberated tends to raise the mold temperature and accelerate the curing reaction. Therefore, the control of the rate of heat generation and the temperature variations during the processing of these materials is very important in order to achieve the desired degree of cure of the product.

The rate of the polymerization reaction is dependent on the temperature and the concentration of monomer and initiator. Since the concentrations of monomer and initiator are established prior to the curing operation, the curing reaction may be more likely controlled by means of controlling the curing environment and cure time.¹ Curing environment can be controlled with a knowledge of the heat transfer during the process and the kinetics of the polymerization reaction.

The kinetic mechanism in almost all thermosetting polymerizations is very similar in nature. Autoacceleration, which is also known as the “gel effect,” is the term used to describe a unique situation which develops in the curing of polyester and other thermoset systems.² As the initial crosslinking occurs, the mobility of the system and the frequency of collisions are rapidly decreased as

* Present address: Materials Research, Cutler-Hammer, Inc., Milwaukee, Wisconsin.

† Present address: Chairman of Chemical Engineering Department, University of Maine at Orono, Orono, Maine.

‡ Present address: Associate Professor, Chemical Engineering Department, University of Maine at Orono, Orono, Maine.

the gel forms. Since the frequency of termination reactions is a function of the rate of their meeting other growing chains, the proportion of termination reactions gradually decreased and the number of addition reactions to other double bonds becomes greater.³ Since more heat is liberated by the addition reactions, the system automatically heats more rapidly as the gel structure becomes tighter and the mobility decreases. This heat, or exotherm, increases the activity of the growing radicals and also speeds the release of more radicals from decomposing initiator, both of which add to the increased frequency of the addition reactions.

Determination of the kinetics, particularly beyond the gel point, is difficult. Indirect methods must be used, since the polymers formed are usually three-dimensional and insoluble. Chemical tests of the extent of crosslinking reaction are definitive to some degree, and bromine absorption⁴ and styrene determination⁵ have been used by some investigators. However, these methods give variable results due to the immobilization of the system at an early stage. Infrared and other spectrographic methods,⁶ electrical conductivity,⁶ dilatometric techniques,⁷ and dynamic mechanical and dielectric methods^{6,8} have all been applied. While some of them include the analysis of the results in terms of the possible mechanisms of polymerization, only physical interpretation of the results have been made.

Recently, application of thermal analysis and calorimetric techniques have seemed to be the most effective method to get complete qualitative and quantitative information on the curing process of thermosets. For this purpose, differential scanning calorimetry (DSC) has been used by a number of workers to study the exothermic heat of cure and the kinetics of curing. However, few attempts have been made to study the curing reaction of polyesters. Horie and his group⁹ investigated the curing reaction of a polyester fumarate with styrene by applying the isothermal techniques of DSC, and they observed a large auto-acceleration in rate of cure and a strong dependence of final conversion on the curing temperature. Kamal and co-workers¹⁰ used DSC to study the curing mechanism of epoxy and polyester systems, and they also proposed an empirical model to describe the cure kinetics of those thermoset systems. Lately, Kubota¹¹ applied DSC to look at the effects of monomer, pressure, low-profile agent, filler, and thickening on the curing of polyesters.

Recently, with the increasing use of SMC and BMC in industry and with the introduction of low-profile polyester resin systems, it has become necessary to have more scientific knowledge for the curing mechanism of these plastics, and further studies are needed.

The primary objective of this work was to develop a kinetic model for the curing reaction of thermoset polyesters by applying the principles of DSC. The present paper discusses the methods and techniques that can be used for such a study and also compares the results obtained to the results of previous studies.

EXPERIMENTAL

Materials

Polyester Resin. A general-purpose polyester resin was selected and used in this investigation. It was supplied by Ashland Chemical Co., Columbus, Ohio. The base polyester resin was prepared using phthalic anhydride, maleic anhy-

dride, and propylene glycol in mole ratios of 2:1:3. As a crosslinking agent, styrene monomer was added to the resin by the supplier. The styrene content has been determined as 28% by weight with an accuracy of $\pm 2\%$ by heating a 5-g sample of fresh resin in an oven at 100°C until a constant weight was attained.

Initiator. A 60% solution of methyl ethyl ketone (MEK) peroxide in dimethyl phthalate (Lupersol DDM) was used. It was supplied by Pennwalt Co., Lucidol Division.

Calorimetric Measurements

The calorimetric measurements were conducted in a DuPont thermal analyzer Model 900 equipped with a DSC cell. A calibration curve was obtained using known values of heat capacities of tin and sapphire and the heats of fusion of tin, indium, and benzoic acid in order to convert the output of the instrument in ΔT into usable calorimetric quantities. The temperature range of the calibration curve was 80 to 200°C.

Exothermic heats of curing reaction were measured by isothermally carrying the crosslinking reaction to completion at a series of different curing temperatures.

A resin sample was catalyzed by mixing it with MEK peroxide (0.7% by weight) for about 1/2 min, and the required amount of sample was weighed into a previously weighed sample pan for each isothermal run. In all measurements, samples were sealed into hermetic containers. The weight of the container with sample was measured before and also after the run to check whether there was any loss of sample during the measurements due to the evaporation of styrene monomer.

After the instrument was prepared for isothermal operation at the desired temperature, the sample and reference containers were introduced into the DSC cell, and the recording of the ΔT output was immediately started. A record of the ΔT output with time was taken until the exotherm curve leveled off to a baseline which was not far from the original baseline. The total area under the exotherm curve was the total heat generated isothermally at temperature T . During the isothermal measurements, the ΔT never exceeded 1.3°C.

Isothermal experiments were performed at 82, 93, 105, and 122°C. At higher temperatures the cure time was of the order of minutes so that the heat absorbed as the sample equilibrated at the cure temperature partially cancelled out the exotherm. Therefore, no reaction was conducted isothermally at higher than 122°C.

At the end of each isothermal run, samples were cooled rapidly and rescanned using a 10°C/min heating rate until no exotherm was observed. Scanning of

TABLE I
Isothermal Heats of Reaction

$T, ^\circ\text{C}$	$Q_T, \text{cal/g}$	$Q_S, \text{cal/g}$	$Q_T + Q_S$
82	42.1	10.2	52.3
93	47.9	6.6	54.5
105	51.4	4.6	56.0
122	63.5	1.6	65.1

samples above the temperature of their isothermal cure was necessary to determine their residual reactivity.

RESULTS AND DISCUSSIONS

Heats of Polymerization

During a vinyl addition polymerization process the conversion of a double bond to a single bond is accompanied by an exothermic heat of polymerization.¹² Removal of this heat often limits the rate at which the reaction can be carried out. Therefore, measurement of the heats of polymerization as a function of time and temperature is one of the most useful methods in determining the rate of crosslinking reaction of thermoset plastics.

It has been already pointed out by a few investigators that the exothermic heat of curing of the polyester resins comes from the following reactions¹¹: (1) the propagation reaction of free-radical crosslinking of the styrene monomer with an active double bond of the unsaturated polyester; and (2) the decomposition reaction of the peroxide initiator. The heat liberated by reaction (2) is negligible compared to reaction (1).

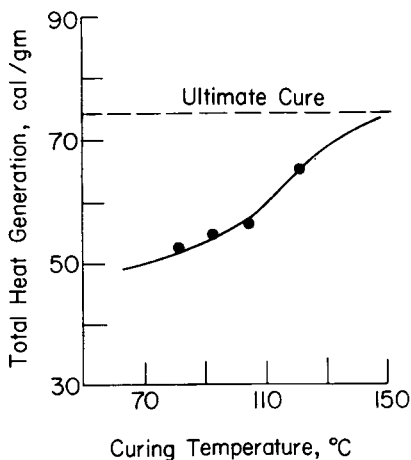


Fig. 1. Total heat generation during cure as function of curing temperature: (●) $Q_T + Q_S$.

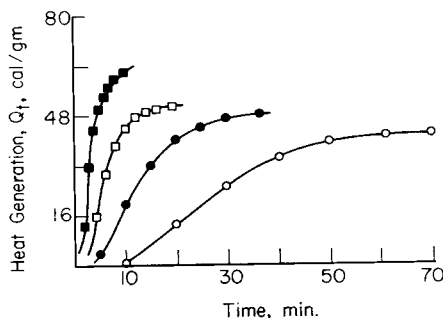


Fig. 2. Cumulative heat evolution during isothermal cure: (■) 122°C; (□) 105°C; (◆) 93°C; (○) 82°C.

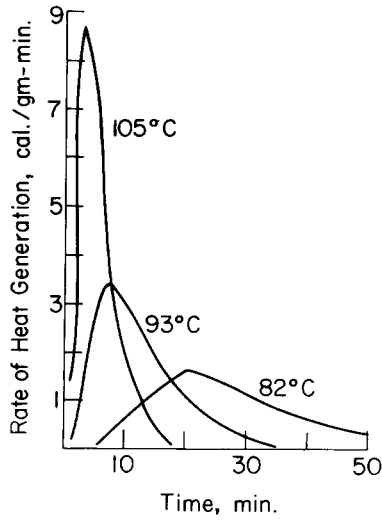


Fig. 3. Rate of heat generation for isothermal cure.

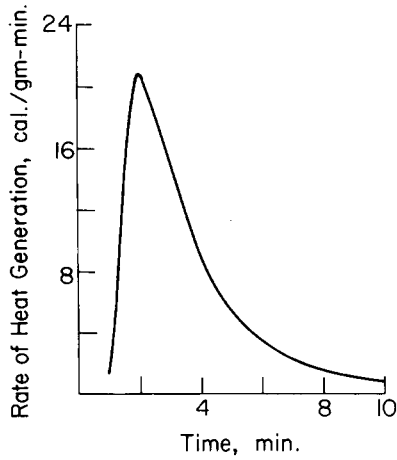


Fig. 4. Rate of heat generation for isothermal cure at 122°C.

It can be reasonably assumed that the exothermic heat generated per unit mass or volume during an isothermal cure is proportional to the number of double bonds reacted in that unit mass or volume. Thus, the measurement of the heat

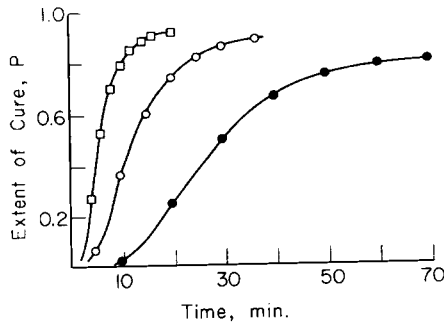


Fig. 5. Extent of reaction during isothermal cure: (●) 82°C; (○) 93°C; (□) 105°C.

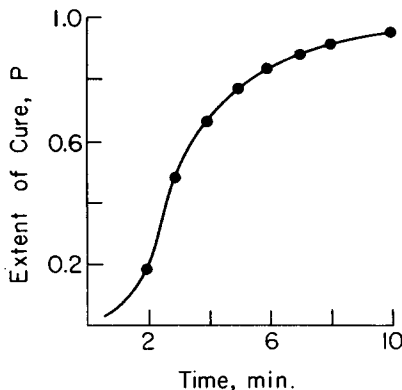


Fig. 6. Extent of reaction during isothermal cure at 122°C.

evolved at any time is a direct indication of the degree of cure (extent of reaction) of the sample at that instant.

The fraction of double bonds reacted during the curing reaction, or the relative degree of cure, P , at time t is defined as

$$P = \frac{Q_t}{Q_T + Q_S} \quad (1)$$

where Q_t is the heat that is evolved isothermally corresponding to a partial cure condition at time t , Q_T is the total heat of reaction that is measured at the end of an isothermal run at temperature T , and Q_S is the heat evolved due to the residual isothermal reactivity of the sample at temperature T (Q_S is determined by heating the sample above its isothermal cure temperature until no exotherm is observed). $Q_T + Q_S$ represent the maximum possible heat of cure at an initial isothermal cure temperature. This quantity cannot be easily measured by a single isothermal run because the reaction becomes highly diffusion controlled at advanced stages of cure and a very long time is required to reach completion under isothermal conditions. This phenomena was also reported in a recently published paper by Kamal and co-workers.¹⁰

Due to the diffusional resistances and because of the restrictions mentioned

TABLE II
Kinetic Parameters

Model
$\frac{dP}{dt} = A \exp(-E_a/RT)P^a(1 - P)^b$
$a = 0.445$
$b = 1.500$
$E_a = 17.04 \text{ kcal/g-mole}$
$A = 2.60 \times 10^9 \text{ min}^{-1}$
Multiple correlation coefficient: 0.9895
Number of data points: 38
Standard error of estimate: 0.0670

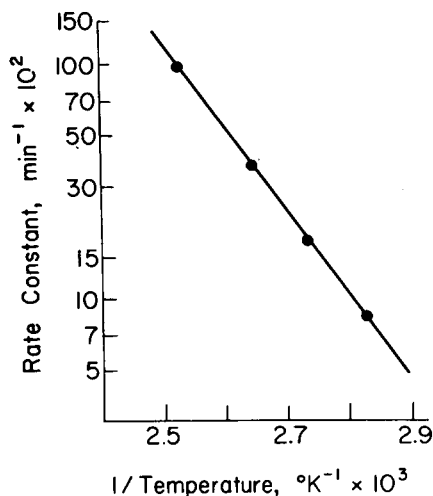


Fig. 7. Arrhenius relation for the kinetic model.

earlier on the temperature limit of isothermal measurements, the upper limit of the total heat of cure could not be measured in this manner. The limit for the total heat of cure was measured by scanning at a constant heating rate of 10°C/min from room temperature to 250°C. The reaction was complete at 180°C, and the total measured heat of cure was 73.9 ± 0.6 cal/g, which is compared with the results of other studies in Table III.

The value of 73.9 cal/g is quite reasonable. The polymerizing mass is 28% styrene and 72% polyester. The polyester has an average degree of polymerization of 12, based on the acid number, which gives a mass per mole of double bond in the polyester of 573 g/g-mole of double bonds. The heat produced by complete reaction of the polystyrene is about 45.7 cal/g (17 kcal/g-mole), and

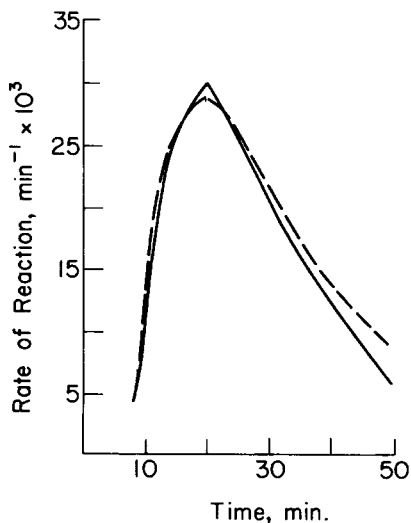


Fig. 8. Comparison between experimental and predicted rate of cure at 82°C: (—) experimental; (---) predicted.

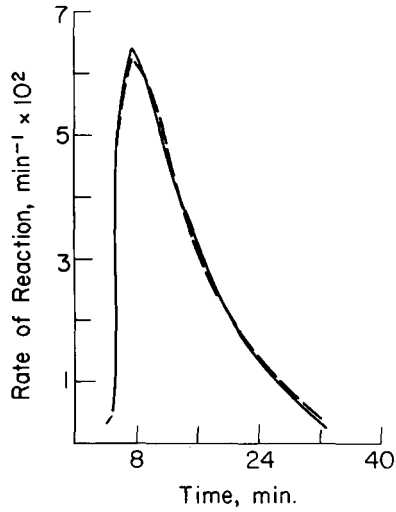


Fig. 9. Comparison between experimental and predicted rate of cure at 93°C: (---) experimental; (—) predicted.

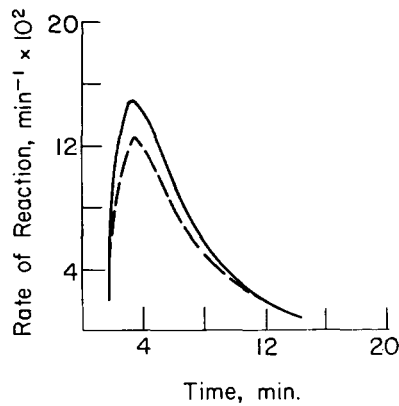


Fig. 10. Comparison between experimental and predicted rate of cure at 105°C: (---) experimental; (—) predicted.

TABLE III
Results of the Curing Studies Reported by Several Investigators

	Kamal and Sourour ¹³	Kamal, Sourour, and Ryan ¹⁰	Kubota ¹¹	Hori, Mita, and Kambe ⁹	Present study
Total heat of cure, cal/g	73 ± 2	83.0	99.5 (630 psi)	—	73.9
Rate constant, min ⁻¹	2.39 × 10 ¹⁰ exp(-18,700/RT)	2.72 × 10 ⁹ (-17,400/RT)	—	—	2.60 × 10 ⁹ exp(-17,040/RT)
Activation energy, kcal/g-mole	18.7	17.4	—	18.5	17.0

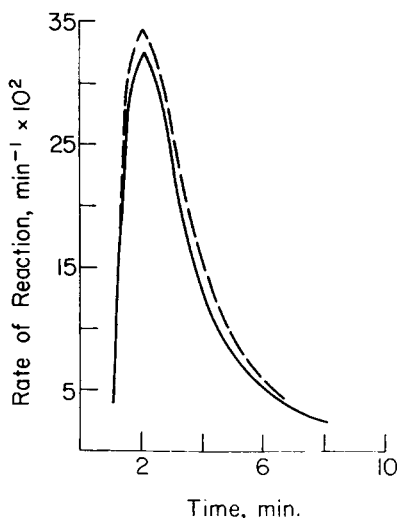


Fig. 11. Comparison between experimental and predicted rate of cure at 122°C: (---) experimental; (—) predicted.

the difference of 28.2 cal/g is attributable to reaction of the double bonds in the polyester. This is equivalent to 22.4 kcal/g-mole, which is not unreasonable for reaction of a double bond by a free-radical mechanism when the double bond is in a resonating, electronegative, hindered environment.

Table I presents the measured isothermal heats of reaction at different curing temperatures. They are also plotted against cure temperature and shown in Figure 1. Isothermal heat generations as a function of time at different temperatures are shown in Figure 2. It can be concluded from the isothermal data that the reaction rate increased and the rate of heat generation increased with increasing temperature (Figs. 3 and 4).

Kinetic Model

Figures 5 and 6 show the extent of reaction, P , as a function of time at different temperatures. Experimental curves of rate of reaction as a function of time have been obtained by using the relation

$$\frac{dP}{dt} = \frac{1}{Q} \left(\frac{dQ}{dt} \right)_T \quad (2)$$

where dP/dt is the rate of reaction, and dQ/dt and Q represent the rate of heat generation and total heat of cure at temperature T , respectively.

A mathematical expression for the curing reaction that could fit all of the experimental data has been developed from studies of different proposed kinetic models. In previous studies it was difficult to predict the kinetics beyond the gel point because of the lack of experimental data. Those studies included only a qualitative analysis of the results or suggested some models based on the n th order kinetics. Recently, it has been reported that such models were not satisfactory because they could not predict the maximum that was observed experi-

mentally in the isothermal rate of reaction curve.¹³ Using this argument, a kinetic equation of the following form was used to fit the isothermal experimental data:

$$\frac{dP}{dt} = kP^a (1 - P)^b \quad (3)$$

where the parameters a and b are constants independent of temperature and k is the rate constant. Dependence of the rate constant upon temperature is represented with an Arrhenius relationship

$$k = A \exp(-E_a/RT)$$

The proposed kinetic model was fitted to the experimental rate data using the computer and a multiple linear regression technique. The results are summarized in Table II. The Arrhenius plot for the rate constants is shown in Figure 7 over a temperature range of 82 to 122°C.

Results from the model revealed excellent agreement with the experimental data over the entire conversion. Figures 8, 9, 10, and 11 show the comparison of the model predicted and experimental rate data.

Finally, the results of the present study were compared to the results obtained by previous investigators and presented in Table III.

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