

Variation of Thermal Conductivity and Specific Heat During Cure of Thermoset Polyesters

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Synopsis

Variation of thermal conductivity and specific heat of a general-purpose unsaturated polyester during cure was investigated experimentally. Measurements were made on the cured, partially cured, and uncured samples, and the results are presented. Both thermal conductivity and specific heat of the cured samples increase nearly linearly with increasing temperature. Effect of degree of cure on the thermal properties is evident during the earlier stages of cure.

INTRODUCTION

Recently, thermoset polyesters have captured many applications in automotive, electrical, and appliance components as a substitute for other, more traditional materials. As a result, the processing of these materials has become very significant in these industries. Like processing of other plastics, the processing of thermosets involves exposure of these materials to varying levels of heat treatment. During such treatment, heat transfer rates are dependent on the curing environment, exothermic heat generation, and the variation of thermal properties during cure.

There are very few reports in the literature concerning studies of the thermal conductivity and the specific heat of thermoset systems. Most of the thermal conductivity studies on crosslinked systems have been conducted on cured epoxy resins, and a linear increase in conductivities of these materials with increasing temperature has been observed by most investigators.^{1,2} In 1964 Hattori³ measured the thermal diffusivity of several linear polymers and a crosslinked polyester as a function of temperature between 10 and 100°C. Recently, Sourour and Kamal⁴ constructed a new apparatus to measure the thermal diffusivity and the thermal conductivity of reactive and nonreactive liquids and solids. They studied the variations in thermal conductivity and diffusivity of a typical epoxy resin during cure. The same authors⁵ also used DSC to study the specific heats of epoxy and polyester systems during cure. However, there are still no informative data reported concerning the variations of thermal conductivity of thermoset polyesters with temperature and degree of cure.

The present paper describes the techniques and methods that can be used to determine the variations of thermal conductivity and specific heat of thermoset polyesters and similar systems and presents the experimental results obtained.

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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. As a crosslinking agent, styrene monomer (28%) was added to the resin by the supplier.

Initiator and Promoter. The peroxide initiator was a 60% solution of methyl ethyl ketone peroxide in dimethyl phthalate from Pennwalt Co., Lucidol Division. The promoter was cobalt naphthenate from Troy Chemical Co.

Thermal Conductivity Apparatus

Thermal conductivity measurements were performed by utilizing a Colora Thermoconductometer. The Colora Thermoconductometer is based upon a method developed by Schroder who gives a detailed description of the method.⁶ Since this apparatus was basically designed for thermal conductivity measurements with solid samples, a new method of sample mounting was developed to be able to measure the thermal conductivities of viscous samples.

The major components of the Colora instrument are a sample system, a heater, and a condenser to collect the vapors from a liquid which is boiled by the heat flowing through a boiling liquid and test sample.

The test sample is fitted between two silver plates which form the upper and lower boundaries of the test sample. After the liquid in the lower vessel begins boiling, the heat flowing through the sample causes the liquid in the upper vessel to boil. The vapor from the upper vessel is condensed and the condensate is collected. After steady state is reached, the time t necessary to distill a fixed amount (1 ml) of the liquid in the upper vessel is measured. If the heat of vaporization of this amount of liquid is Q , the thermal conductivity k is then given by

$$k = Qh/At(T_A - T_B) \quad (1)$$

where h and A are the thickness and cross-sectional area of the sample and T_A and T_B are the boiling temperatures of the lower and upper liquids, respectively. According to eq. (1), the thermal resistance of the sample, R , is given by

$$R = t(T_A - T_B)/Q \quad (2)$$

where

$$k = h/RA \quad (3)$$

In this investigation three different pairs of liquids were selected (Table I) to measure the thermal conductivities at different temperatures. Calibration diagrams (R vs t) for each liquid pair were obtained using three glass samples which had different thicknesses.

In order to determine the variation of conductivity with temperature and degree of cure, the measurements with polyesters involved the following forms of samples: (a) uncured resin; (b) partially cured resin; (c) cured resin.

The most important step prior to the measurements was the preparation and handling of the test samples. A new sample-handling technique was developed

TABLE I
Selected Liquid Pairs for Thermal Conductivity Measurements^a

Liquid A	Liquid B	T_A , °C	T_B , °C	T_M , °C
Carbon disulfide	ether	46.3	34.6	40.5
Ethyl acetate	methanol	77.0	64.2	70.6
Water	trichloroethylene	100.0	87.0	93.5

^a T_A = boiling temperature of liquid A; T_B = boiling temperature of liquid B; T_M = measuring temperature $(T_A + T_B)/2$.

for the samples of uncured and partially cured resins which were highly viscous materials. Uncured and partially cured samples were embedded in cylindrical rings that were prepared from a cured polyester sample. In order to maintain the samples inside the rings and in good contact with the silver plates, the top and bottom of the rings were covered with very thin Teflon sheets. Such a sample system required the development of a new method of calculation because of the additional complication of the new sample system. The Colora Thermoconductometer was basically designed for measurements with solids, and its original sample system contained only the test sample. However, in the new system developed in this work, the conducting sample system did not have homogeneous surfaces. Conductivity of the cylindrical ring which holds the test sample had to be also considered. Therefore, the measured resistance of the total sample system, R_s , involved the thermal resistances of the embedded material, R_m , and the ring, R_k . Since the surfaces of the sample were most effectively kept at constant temperature through heats of vaporization of liquids, the entire cylindrical surface was maintained at a fixed temperature, the radical heat losses were considered to be negligible, and then each surface plane of the sample was isothermal. Since the embedded samples were highly viscous, it was also assumed that the convective effects were negligible.

Consequently, the conductances $1/R_m$ and $1/R_k$ of the two materials were additive, and then

$$1/R_s = 1/R_m + 1/R_k \quad (4)$$

With the values of thermal conductivity, cross-sectional area, and height of the ring, the resistance of the ring, R_k , was calculated from

$$R_k = h/R_k A \quad (5)$$

The thermal resistance of the test material was calculated using eq. (4). That is,

$$R_m = R_s R_k / (R_k - R_s) \quad (6)$$

In some measurements where thin Teflon sheets were used as the interfaces between the silver plates and test sample, the conductivity of the Teflon sheets was also taken into account in calculating the actual R_m .

Partially cured samples were obtained by inhibiting the crosslinking reaction of a catalyzed sample just before gelation. As an inhibitor, a small amount of hydroquinone solution was used. Partially polymerized samples maintain their form for 2 to 3 hr and up to 70–80°C. Further reaction of these samples was observed when they were subjected to higher temperatures.

Calorimetric Measurements

The calorimetric measurements to measure the specific heats were conducted in a du Pont thermal analyzer Model 900 equipped with a DSC cell. A calibration curve was obtained using known values of heat capacities of tin and sapphire in order to convert the output of the instrument in ΔT into usable calorimetric quantities.

In all measurements samples were sealed into previously weighed hermetic containers. Measurements were conducted in an air atmosphere with a $10^\circ\text{C}/\text{min}$ heating rate, and empty sample containers were used for the reference system.

RESULTS AND DISCUSSIONS

Thermal conductivity measurements of cured polyester samples were made after they had been postcured at 90°C for 3 hr. This was necessary to prevent any further postcuring during the measurements. Measurements at different temperatures were repeated at least twice in order to obtain reproducible results. Thermal conductivities of a cured polyester are plotted against temperature in Figure 1. A linear increase in conductivity with increasing temperature from a value of 4.5×10^{-4} cal/cm-sec- $^\circ\text{C}$ at 40°C to 5.0×10^{-4} cal/cm-sec- $^\circ\text{C}$ at 94°C was observed.

The variation of thermal conductivity with degree of cure was observed by determining the conductivities of fresh and partially cured resins over the same temperature range in which the measurements on cured samples were performed. The results of these measurements were given in Table II. The primary objective of these measurements was to characterize the behavior of thermal conductivity

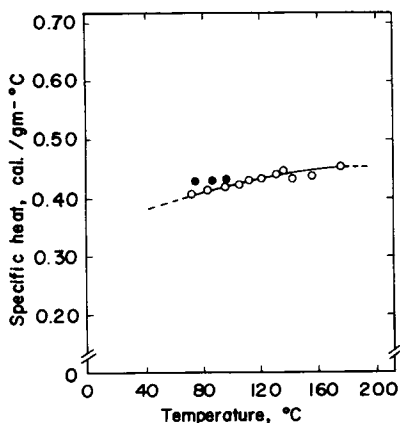


Fig. 1. Specific heat of cured polyester: (●) uncured resin; (○) cured resin.

TABLE II
Thermal Conductivity Data

Sample	Thermal conductivity, 10^{-4} cal/sec-cm- $^\circ\text{C}$		
	40.5 $^\circ\text{C}$	70.6 $^\circ\text{C}$	93.5 $^\circ\text{C}$
Uncured	2.5-3.0	4.9	4.5
Partially cured	4.5	4.6	3.7
Cured	4.5	4.8	5.0

during cure. The results showed that the conductivity increased as the material cured. However, the values determined for the partially cured samples did not show a regular relationship with temperature due to the exothermic nature of the samples. Therefore, a complete correlation of the thermal conductivity with temperature during cure could not be developed.

The specific heats of cured polyester samples have been determined over the temperature range of 60–180°C with an accuracy of about 1%–2%, and the results are shown in Figure 2. A nearly linear increase in specific heat with increasing temperature between 60° and 120°C was observed, and the values of above 120°C did not change significantly.

Warfield and his co-workers⁷ have noted the existence of a possible glass transition at 126°C upon heating these materials. Only a limited amount of data is available in the literature concerning these transitions in thermosetting polymers, although these transitions are particularly significant because of their relationships to the mechanical and electrical properties of the polymers. Studies to determine the existence of such transitions were then undertaken in this investigation. A slight change of slope near 120°C on the DSC heating curves suggested the probable existence of a second-order transition in this range. In the thermomechanical analysis (TMA) of the cured samples, one of the samples showed a definite transition with the point of inflection at 116°C. However, an abrupt increase in specific heat at this presumed transition has not been observed. Therefore, it was reasonably concluded that these polymers did not undergo a sharp transition upon heating over the range used here. This was attributable to the highly crosslinked structure of these materials. Crosslinking reduces the probability of low frequency vibrations of the polymer chains as well as the probability of further structural change.⁷

On the other hand, DSC heating curves showed a sharp exothermic transition at 210°C. That was due to the thermal degradation of these materials above this temperature, which has also been verified by TGA.

The specific heat of uncured resin was measured by heating an uncatalyzed polyester sample in the DSC cell, and it was found to be 0.43 cal/g-°C over the temperature range of 70–100°C. The samples began to cure due to thermal copolymerization when heated above 100°C.

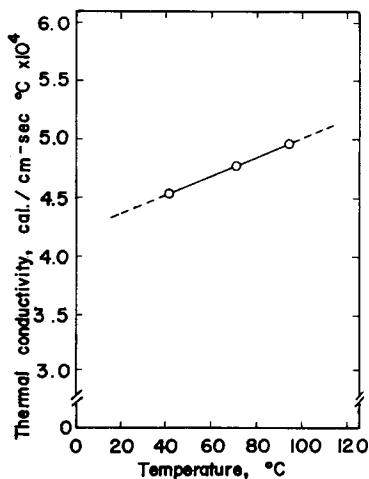


Fig. 2. Thermal conductivity of cured polyester.

In order to evaluate the variation of specific heat during the polymerization reaction, the mathematical procedure that was suggested by Kamal and Sourour⁵ was followed. They reported that the variation in specific heat of a thermoset system during cure can be predicted from a DSC scan of an uncured material by using the following energy balance:

$$C_p(P,T) \frac{dT}{dt} = \dot{Q}_s(T,a) - \dot{Q}_r(P,T) \quad (7)$$

where C_p is the specific heat of the sample which is dependent on the temperature and degree of cure, P ; \dot{Q}_r is the rate of heat generation during cure; and \dot{Q}_s represents the measured rate of heat input to the sample. Values of \dot{Q}_s include the heat of reaction and the heat required to raise the sample temperature during DSC scanning. Since the heating rate dT/dt (or a) was constant during heating of a sample, the above equation could be applied to determine the variation of specific heat during cure. Values of the rate of heat generation were obtained from the isothermal cure data that were reported previously from this laboratory by the same authors.⁸ The predicted values of specific heat at 100 and 122°C were almost of the same order of magnitude as the values that were predicted for the cured samples at those temperatures.

Specific heats below 100°C showed a different behavior from the values of a cured sample. That suggested that the degree of cure could affect the value of specific heat of polyesters during the earlier stages of cure.

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