A DSC Kinetic Study of the Epoxy Network System Bisphenol-A diglycidylether- Bis(4-aminocyclohexyl)methane

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SUMMARY

The kinetics of the curing reaction of an epoxy resin based on bisphenol-A diglycidylether with a cycloaliphatic diamine, bis(4-aminocyclohexyl)methane, was studied by differential scanning calorimetry. The measurements were performed both under isothermal conditions and as a function of heating rates. The reaction was also followed by determining the Tg of the resin cured for different time intervals at 150°C. The enthalpy of the reaction was derived from these measurements. The rates and extent of cure were determined. The cycloaliphatic amine used for this study was demonstrated to be more reactive than analogous aromatic systems and yet provided rigid networks with a desirably high Tg.

INTRODUCTION

Our early work[1] has shown, as one might expect on basicity considerations, that cycloaliphatic amines are much more reactive than their aromatic counterparts and still can provide for a rigid, high Tg epoxy network. Moreover, they also have a comparatively long pot-life and relatively low viscosity at mixing temperatures of 50-60°C. Therefore, one may anticipate that their importance should increase in the various industrial applications of these important thermosets. The morphology and final properties of epoxy resins which are widely used as matrices for various composites strongly depend on the state and extent of cure of the resin. Clearly, knowledge of curing kinetics of the resin with the amine of choice is necessary in order to achieve optimum mechanical properties and consistent quality of the final product.[2,3]

In the present work, the curing kinetics of a bisphenol-A diglycidylether (EPON 828) and bis(4-aminocyclohexyl)methane (PACM-20) were studied in stoichiometric mixtures for the temperature range 80-150°C by differential scanning calorimetry. Profiles of the time and temperature dependence of cure were obtained and the heat of reaction was calculated. Also the variation of Tg with cure time was investigated at 150°C.

EXPERIMENTAL

The epoxy resin used was Shell Epon 828 which had an epoxide

equivalent weight of 190 gm/equivalent. The cycloaliphatic di-
amine bis(4-aminocyclohexyl)methane (PACM-20) is a product of
DuPont and used as supplied.

The kinetic measurements were conducted with DSC-2 differen-
tial scanning calorimeter. The DSC cell was swept with a flow of
dry, oxygen-free nitrogen gas at a pressure of 20 psi during the
reactions. Stoichiometric mixtures of the resin and the amine
were sealed in aluminum pans (8-15 mg sample/pan) and examined
under dynamic (constant increasing rate of temperature rise) or
isothermal conditions. A sample of indium was used as a standard
for the calorimetric calibration of the instrument. The amount
of heat liberated during the reactions were calculated by weigh-
ing the chart paper covering the peak area on a four place ana-
lytical balance.

For isothermal measurements, the sample was inserted into
the cell at 50°C and then the temperature of the system was in-
creased to the desired temperature with a heating rate of 160°K/
min. Tg of the samples kept in an oven at 150°C for different
time intervals were determined via DSC using a heating rate of
10°K/min.

RESULTS AND DISCUSSION

Thermally scanning an epoxy resin-diamine mixture at a con-
stant rate produces a characteristic exothermic peak in heat flow
due to the curing reaction. A typical scan for our system at a
heating rate of 5°K/min is shown in Figure 1.

FIG. 1

DSC SCAN FOR RESIN CURE
AT 5°K/min. HEATING RATE
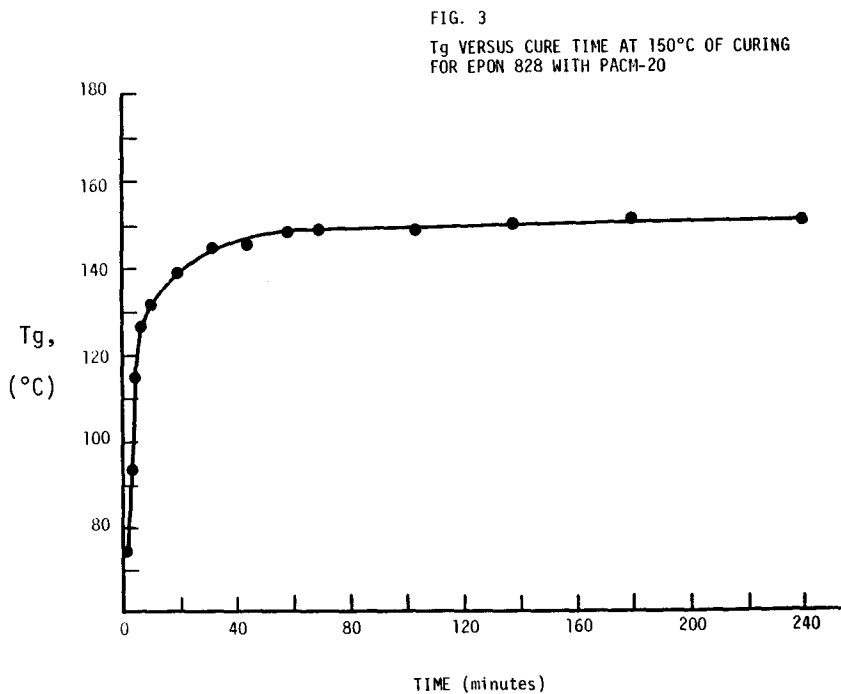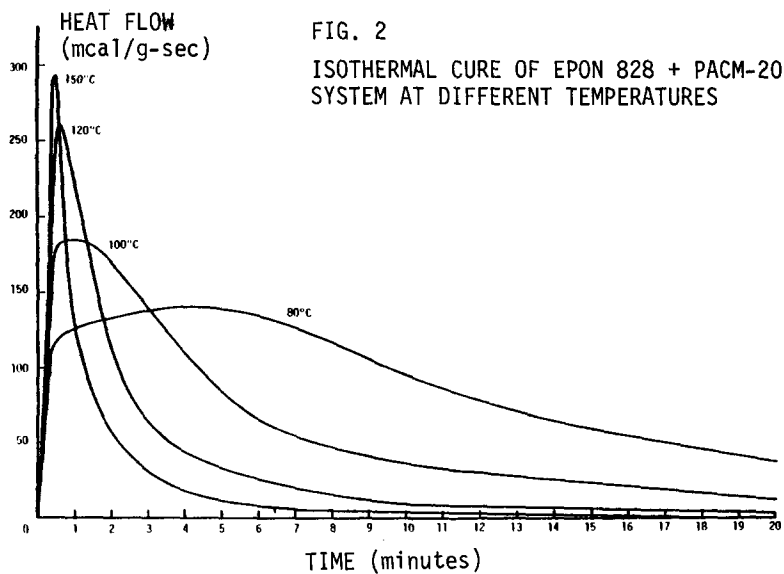(EPON 828 + PACM-20)
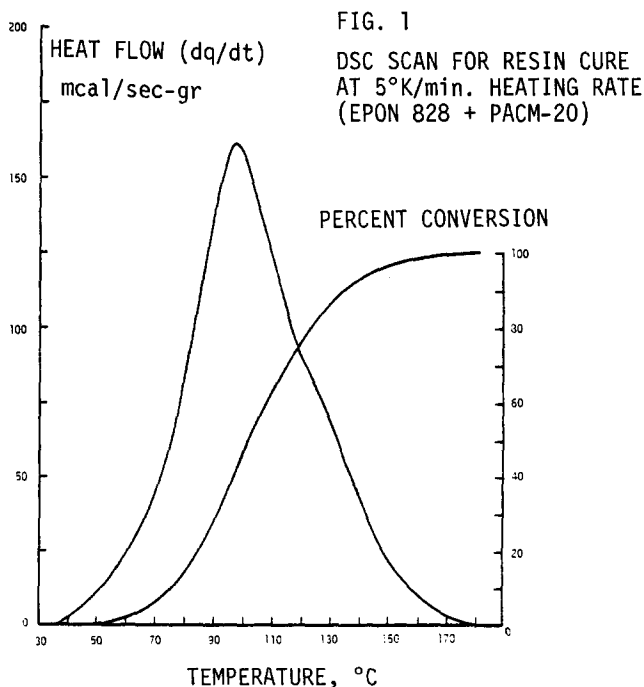
TEMPERATURE, °C

Also shown is the percent conversion plotted against temperature.
Percent conversion was calculated at $(q_T/q_0) \times 100$ where q_T is
the area under the heat flow versus temperature curve up to temp-
erature T and q_0 is the total peak area. Values for the heat of
the curing reaction, q_0, from several scans at different heating
rates are given in Table I.

TABLE I
Heat of the Curing Reaction from Area under the
DSC Exotherm Peak

Heating Rate ^{o}K/min.	Peak Area, g. J/g	T_i ^{o}C	T_p ^{o}C	T_f ^{o}C
2.5	362.2	30	85	164
2.5	373.4			
5	402.7	35	97	180
5	396.8			
10	418.8	45	113	215
10	408.5			

$\overline{\Delta H}$ = 393.7± 21.7 J/g

The mean value is 393.7 ± 21.7 J/g. Also included in Table I is
the temperature at the start, maximum and end of the curing re-
action exotherm peak, T_i, T_p, and T_f, respectively. As expected,
the data show a trend towards higher temperatures with increasing
heating rate due to the activation energy effect.
    Isothermal curing reactions were conducted at 80, 100, 120,
and 150°C with the samples subsequently held in the DSC until cure
was apparently complete as determined by the development of a con-
stant baseline. These curves are plotted in Figure 2. The data
were obtained by extrapolating the final baseline back to intersect
the initial exotherm. The percent conversion may be obtained as
described before, except the q_0, the heat evolved for complete re-
action must be taken as the average value from the dynamic scans.
This is due to the slow diffusion and hence reaction of the end
groups at lower temperatures.[4,6]
    As is well known, another method to determine the curing of
an epoxy resin is to follow the increase in the Tg of the system
as a function of cure time.[5] The time corresponding to the begin-
ning of the plateau in Tg versus Time curve corresponds to the
"complete" curing. For our system such a curve at 150°C is given
in Figure 3. It shows that the reaction is essentially complete
in approximately 50 minutes. This latter method yields a somewhat
higher value than the former one. This is due to the reduced
sensitivity of the instrument in the isothermal curing mode when
high conversions are reached and the heat evolved becomes very
low. We did investigate higher reaction temperatures to prove

HEAT FLOW
(mcal/g-sec)

FIG. 2

ISOTHERMAL CURE OF EPON 828 + PACM-20
SYSTEM AT DIFFERENT TEMPERATURES

300

150°C

250

120°C

200

150

100°C

100

80°C

50

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

TIME (minutes)

FIG. 3

Tg VERSUS CURE TIME AT 150°C OF CURING
FOR EPON 828 WITH PACM-20

180

160

140

Tg,

120

(°C)

100

80

0   40   80   120   160   200   240

TIME (minutes)

that the Tg plateau was not an artifact related to chain end immobilization.

Our work on the analysis of the kinetic results and mechanism is continuing.

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