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DETERMINATION OF CURE SCHEDULES OF EPOXIES BY DIFFERENTIAL SCANNING CALORIMETRY

R. Thiagarajan, P. V. Reddy, S. Sridhar and *M. C. Ratra*

INSULATION DIVISION, CENTRAL POWER RESEARCH INSTITUTE, BANGALORE 560 012, INDIA

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The dynamic DSC method, which utilizes the variation in peak exotherm temperature with heating rate, is used to measure the energy of activation for anhydride cured bisphenol-A epoxy and epoxidized novolak systems. Kinetic parameters are also determined for B-stage glass fabric reinforced epoxy novolak hardened with precursor novolak. Using the expression developed for life estimation of wire enamels by Toop, probable cure schedules are evaluated. The results are compared with glass transition temperature measured under isothermal conditions. It is inferred that the Toop's equation of thermal index can be used to derive reliable cure schedules of epoxies with relative improvement in speed and ease.

Differential Scanning Calorimeter (DSC) which measures the heat flow to the sample as a function of temperature directly, rapidly and accurately has been extensively used to study the cure kinetics of various thermosets. This method requires small quantity of sample and the measured value of heat of polymerzation is uncomplicated by complex changes in physical state (liquid-solid) which accompany curing and therefore correlates directly with progress of chemical reaction [1-9].

Ozawa's method [10] based on the variable programme rate has been commonly used to derive kinetic parameters for many industrial materials and forms the basis of the ASTM method on Arrhenius Kinetic Constants for Thermally Unstable Materials [11]. The present paper examines the possibilities of extracting data on cure schedule of epoxies by fitting the kinetic data into the mathematical expression developed by Toop [12] that relates activation energy to time by temperature.

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Experimental

Materials

Commercial diglycidyl ether of bisphenol-A (DGEBA) of epoxy content 5 - 5.4 mol epoxy/kg (viscosity 9000 - 13000 cps at 25°) and modified carboxylic acid anhydride of anhydride content 94% (viscosity 150 - 230 cps, at 25°) of CIBA-GEIGY were used as supplied.

Multifunctional epoxy novolak was prepared by controlled reaction of epichlorohydrin and phenolic novolak in basic medium. Benzene was added to the resin and the by-product, sodium chloride, was removed by filtration. The solvent was distilled off under vacuum to form high viscous product (5000 - 6000 cps at 100°) of epoxy content 3.4 - 4 mol epoxy/kg.

Precursor novolak of molecular weight 400-450 was also used as curing agent. It was synthesized in the presence of acid catalyst with formaldehyde and phenol in the mole ratio less than 1.

Impregnation

Epoxy novolak and precursor novolak were mixed in proper molar ratio. The required viscosity was obtained by addition of methyl ethyl ketone. Glass cloth was passed through the dip tank containing the resin solution. After passing between two adjustable squeeze rolls, the impregnated cloth was dried at room temperature overnight and then at 65° for 20 minutes. The initial viscosity of the resin solution was adjusted in such a way as to achieve impregnation with an average resin content of about 40% by weight. The B-stage material was stored at -10° during the period of experiment.

Measurements

Thermal data was generated with Perkin-Elmer DSC-2C coupled with thermal analysis data station (TADS).

About 5-10 mg prepolymer samples were used for each run. Circular discs of impregnated glass cloth that fit into sample pans were layered to the sample weight of the order of 10 mg. Powdered samples of cured material were preferred for the determination of glass transition temperature. The experiments were conducted in inert atmosphere by purging dry nitrogen to prevent possible oxidation at elevated temperatures.

Thermal behaviour was examined for the following uncured systems:

[a] premix of DGEBA and acid anhydride hardener
[b] premix of epoxy novolak and acid anhydride hardener
[c] B-stage glass cloth impregnated with epoxy novolak
and precursor novolak.

Results and discussion

Resin-hardener stoichiometry

The evaluation of kinetic data from dynamic scans of DSC is illustrated by considering curing of bisphenol-A based epoxy resin with anhydride hardener. As the prepolymer was heated, chemical crosslinks were set up to form a rigid structure, resulting liberation of heat, ΔH, from the sample as an exothermic peak. Different concentrations of resin and hardener mixture were scanned at a particular heating rate (40 deg/min) and the heat of reaction was plotted against molar ratio of the reactants (Fig. 1). The data show an orderly increase in DH with hardener/resin ratio upto 1 and then there was a fall above this value. Based on these results the resin-hardener stoichiometry was maintained 1:1 throughout this study.

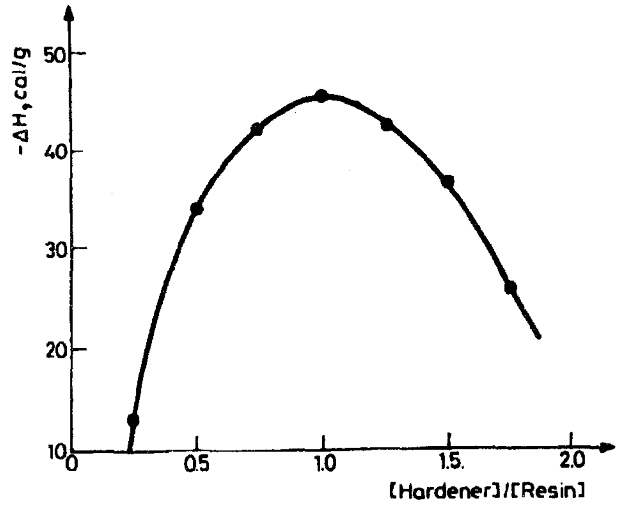

Fig. 1 Change of heat of reaction with concentration of hardener

Order of the reaction

In principle a single DSC profile at a constant scan rate, β is sufficient to define the kinetic order of the reaction by using the expression

$$k = \frac{\Delta H^{n-1}\ \mathrm{d}H/\mathrm{d}t}{(\Delta H - H_p)^n}$$

where k is the rate constant, dH/dt the height of the ordinate of DSC exotherm profile at a particular temperature T, H_p the partial heat of the reaction and n the kinetic order of the reaction. Since the majority of reactions follow orders from 0.5 to 2.5, the recommended procedure is to substitute these values in the above equation and to find the best linear regression fit of log k on inverse absolute temperature. Typical plots are shown in Fig. 2 where the linearity is maintained when $n = 1$. It is verified that similar plots at other heating rates also exhibit identical trend when the order is assumed unity.

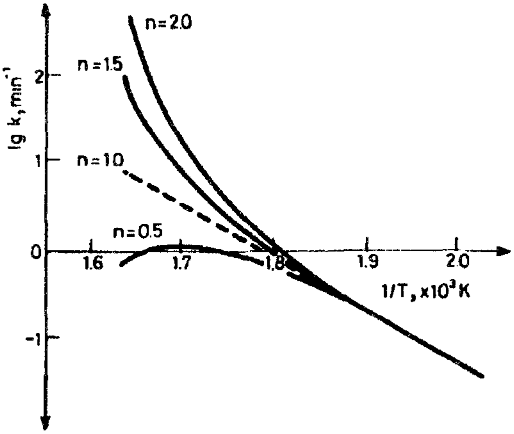

Fig. 2 Order of the reaction from single dynamic DSC trace at 40 deg/min heating rate

Energetics of the reaction

By scanning samples at different heating rates, a series of curves as shown in Fig. 3 were obtained, the peak temperature moving to lower values

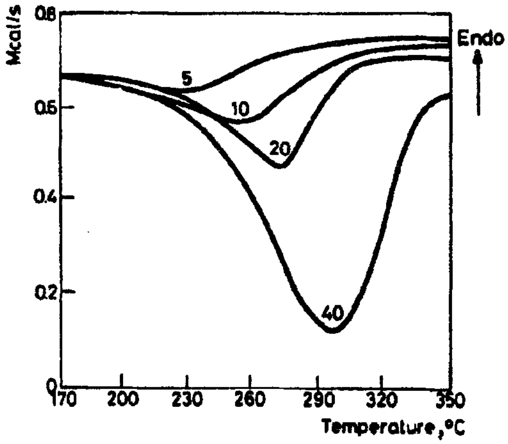

Fig. 3 Variation of peak temperature with program rate

with reduced scan rate. From these traces, the degree of conversion, α, was calculated at various temperatures using the equation

$$\alpha = H_p / \Delta H$$

and the results are shown in Fig. 4. It is observed that the extent of the reaction at the peak temperatures is around 0.5 and is independent of heating rate for a particular system. Similar observations were made by several authors [1-10]. Based on this fact, a relationship connecting peak temperature, T_p and heating rate, β, has been derived [10,12,13].

$$-\log \beta - 0.457 \frac{E}{R} (1/T_p) = \text{constant}$$

The slope of the plot log (heating rate) versus $1/T_p$ furnish the overall activation energy of 17.4 Kcal/mol. The pre-exponential factor, A was calculated from the equation [14]

$$A = \frac{\beta E}{R T_p^2} \exp (E / R T_p)$$

which was found to be $5\text{x}10^6$ - $6\text{x}10^6$ min^{-1} at different heating rates tested.

Data can further be generated from Fig. 4 to draw Arrhenius plots as seen in Fig. 5 at varied degrees of conversion. No appreciable change in slope is observed, thus confirming that the mechanism remains same throughout the curing process.

Evaluation of curing condition

Notable reports on the application of thermal analysis for estimation of thermal life of wire enamels from the decomposition reactions are found in literature [12, 15-17], which is based on experimentally determined relationship between time to failure and appropriate variable that induce the failure. The most common exercise is to measure activation energy by a series of runs at different heating rates and to monitor the decay of a selected physical property with time to lead relevant failure criterion, according to ASTM D 2307. Accordingly a mathematical expression, based on life theory and thermogravimetric theory, has been developed [12].

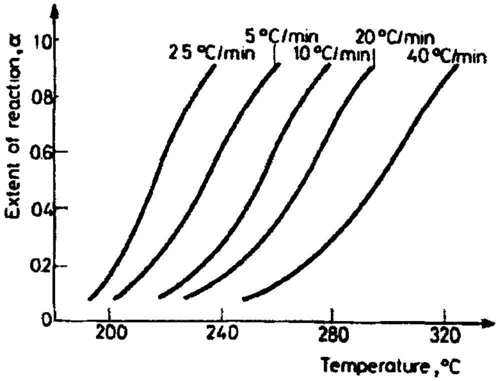

Fig. 4 Extent of reaction vs. temperature

$$\log T_f = \frac{E}{2.303 R\,\theta} + \log \frac{E\,p\,(x_f)}{R\beta}$$

where $\log p(x_f)$ 155 -2.315 - 0.457 E/RT

E = energy of activation
R = gas constant
T = temperature at which specific change is observed
β = heating rate

θ = thermal condition
T_f = time to condition at temperature, θ

Because of the simplicity and reliability it is commonly the preferred technique of thermal rating where thermal degradation is the result of simple chemical reaction.

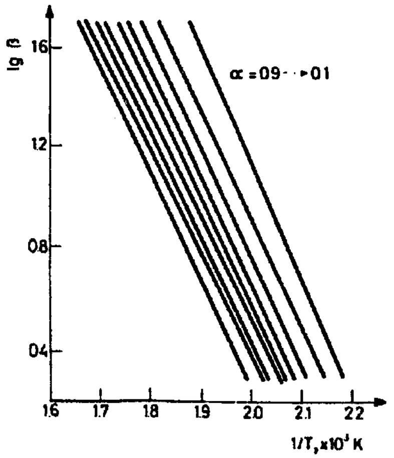

Fig. 5 Activation energies at different fraction of reaction

The curing process is also due to chemical reaction with no change in mechanism like thermal degradation of polymers, the final cure temperature values derived from DSC trace was substituted in finding x_f. Numerically evaluated values of log $p(x_f)$ were tabulated [12, 18] from which $p(x_f)$ was deduced. The unknown quantities were read out from thermograms and fitted into the above equation. Different values of θ at which curing was carried out was substituted to get T_f. For doing this, thermograms obtained at particular range of heating rates were considered. According to Fava [1], at slow heating rates (less than (2deg/min) some of the initial and final reactions go unrecorded because of lack of instrument sensitivity and fast scanning rate (above) 20deg/min) give rise to thermal inertia and hence distorted thermograms. Hence the curing conditions were estimated using isotherm profiles run at scanning rates between 2.5 deg/min and 10 deg/min.

The range of T_f values are summarized in Table 1. The cure schedule of the system by this procedure is more precise and falls within the wide range of values found in product catalogue [19].

Table 1 Cure schedule of epoxy resin with anhydride hardener

Cure Temperature °C	Cure schedule in hours	
	Present work	Literature value
200	1.2-1.4	1-2
180	2.6-3.2	2-5
160	6.5-7.5	5-10
140	17-20	>20

The kinetic data and curing conditions for epoxy novolak resin with anhydride hardener (ENAH) and glass fabric reinforced epoxy novolak cured with precursor novolak (GREN) are presented in Table 2. Epoxy novolak resin, because of multifunctional reactivity, cures much faster with anhydride hardener compared to difunctional diglycidyl ether of bisphenol-A with the same hardener, which effects curing in shorter period only at enhanced temperatures. Glass laminate system, however, behaves different with precursor novolak hardener requiring more time for curing compared to ENAH as is evidenced by higher energy of activation.

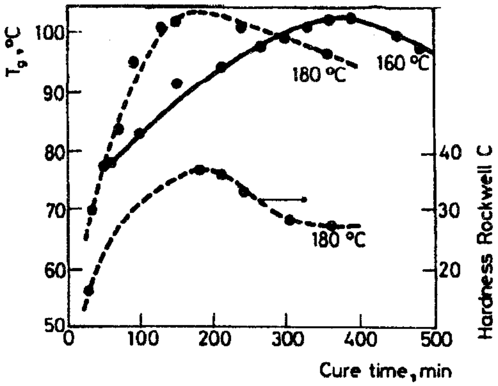

Fig. 6 Change of Tg and Rockwell C hardness with extent of cure

Glass transition temperature

A normal conventional practice to establish cure schedule for thermoset is based on ASTM D 648-56 method which measures heat distortion temperature. Calibrating glass transition temperature, T_g of epoxies by DSC against this standard procedure, Fava [1] found a good correlation between them and recommended the measurement of T_g as a simpler and more versatile alternative to the conventional method. Thus measurements of T_g were made for resin-hardener mass (system a) oven aged at 160° and 180° at regular intervals of time to prove the validity of Toop's equation for studying cure schedule. The results are illustrated in Fig. 6. There was a rapid increase in T_g until about 6.5 and 3 hours for the samples cured at 160° and 180° respectively beyond which the values fell off. The results agree with the view that the gradual increase occurs as long as crosslinking takes place.

Table 2 Kinetic data and cure schedule for ENAH and GREN

Kinetic data	ENAH	GREN
Reaction order	First	First
Energy of activation, kcal /mol	15.7	22.5
Pre-exponential factor, min^{-1}	(3-3.7) 10^6	(1.5-2)10^{10}
Rate constant at 180°C, min^{-1}	0.08-0.10	0.22-0.28
Time to cure in hours		
at 200°C	0.30-0.33	0.27-0.28
180°C	0.63-0.70	0.78-0.81
160°C	1.42-1.55	2.45-2.57
140°C	3.45-3.75	8.75-9.15

This insures that the product has sufficiently been cured around that period and the diminishing values are suggestive of degradation. The cure conditions established by this conventional method is in excellent agreement to the present study. similar observations were made when Rockwell C hardness was monitored as a measure of extent of cure, and hence this lends confidence in using Toop's expression in evaluating cure schedules of epoxies.

Conclusions

Dynamic scans utilize the variation in peak exotherm temperature with heating rate and offer a precise evaluation of activation energy. By fitting these data into the equation developed by Toop for determining thermal index of wire enamels, probable cure schedule with better accuracy has been obtained for epoxy resin with anhydride hardener. The validity of the technique is proved with the data obtained from conventional procedures. Although this study is concerned with epoxies, the method may be adopted to optimize cure cycles for other thermoset reactions also where the reaction mechanism does not change throughout the curing process.

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Zusammenfassung - Mittels DSC wurde die Energie zur Aktivierung von anhydridgehärteten Bisphenol-A Epoxy- und epoxydierten Novolack-Systemen bestimmt. Kinetische Parameter wurden auch für glasfasergewebe-(B-Zustand)-verstärkte, mit Präkursor-Novolack gehärtete Epoxy-Novolacke bestimmt. Unter Anwendung der von Toop entwickelten Beziehung für die Lebensdauer von Drahtlack wurde der vermutliche Härtungsablauf aufgestellt. Diese Ergebnisse wurden mit unter isothermen Bedingungen bestimmten Werten für die Glasumwandlungstemperatur verglichen. Es wid festgestellt, daß die Gleichung von Toop zu einer schnelleren und einfacheren Ermittlung von zuverlässigen Härtungsabläufen geeignet ist.