Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Shelf-Life Studies on B-Stage Novolac Epoxy Glass Mica Tapes

Vimala Sitaraman[a]; P. G. Agashe[a]; K. M. Kamath[a]; S. Sankaralingam[b]; K. Kishore[b]
[a] BHEL Corporate R & D Division, Hyderabad, India [b] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

To cite this Article Sitaraman, Vimala , Agashe, P. G. , Kamath, K. M. , Sankaralingam, S. and Kishore, K.(1983) 'Shelf-Life Studies on B-Stage Novolac Epoxy Glass Mica Tapes', Journal of Macromolecular Science, Part A, 19: 2, 225 — 237

To link to this Article: DOI: 10.1080/00222338308069437

URL: http://dx.doi.org/10.1080/00222338308069437

J. MACROMOL. SCI.–CHEM., A19(2), pp. 225-237 (1983)

Shelf-Life Studies on B-Stage Novolac Epoxy Glass Mica Tapes

VIMALA SITARAMAN, P. G. AGASHE, and K. M. KAMATH

BHEL Corporate R&D Division
Hyderabad, India

S. SANKARALINGAM and K. KISHORE

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore, India

ABSTRACT

Activation energy for the curing process of epoxy glass mica tape has been experimentally determined from differential scanning calorimetric measurements and found to be 20 kcal/mol. Thermochemical calculation shows that the rate controlling step is the dissociation of the C–O bond in the epoxide leading to ring opening and its subsequent reaction with amine hardener. Shelf life has been determined from the measurement of the enthalpy loss corresponding to the curing during the aging process. The kinetics of the aging process also yields an activation energy of 20 kcal/mol which corresponds to the slow curing of the epoxy resin.

0022-233X/83/1902-0225$3.50/0

INTRODUCTION

Main insulation in heavy electrical machines comprises of epoxy glass mica tape in which novalac epoxy resin in the B-stage acts as a binder. The B-stage resin is partially cross-linked in nature. This on consolidation at 150-160°C under pressure gives voidless insulation around a copper conductor. This B-stage resin undergoes cross-linking continuously, the extent of which depends on the conditions of storage. In a tropical country like India this poses a serious problem because the temperature fluctuation is large. Since the material is procured from abroad, during transit and transportation the material is subjected to varying environmental stresses. This was found to shorten the specified shelf life and sometimes adversely affects consolidation.

In the manufacture of epoxy glass mica tape, novolac epoxy resin is brought to the B-stage at elevated temperatures. When these tapes are stored between 5 and 20°C, they retain a certain amount of partially cross-linked resin in the B-stage for a period ranging between 6 and 12 months. The extent of cross-linking of B-stage tapes thus decides the life of the material. The conventional method of assessing the usefulness of a tape is by measurement of resin flow under specified conditions of pressure and temperature. This is highly subjective and does not give any indication of alterations needed in processing conditions because of the advancement of the B-stage.

The objective of the present investigation is to understand the kinetics and the mechanism of the curing process and to predict the shelf life of the tape from accelerated aging studies.

EXPERIMENTAL

Sample

Epoxy glass mica tape with an average resin content of 40% by weight, sandwiched between glass and mica, was used.

Instrument

A DuPont 910 Differential Scanning Calorimeter (DSC) along with a 990 programmer module was used.

Dynamic DSC runs were carried out at heating rates 2, 3, 5, and 10°C/min according to the manufacturer's instruction. The sample was prepared by cutting the tape in the form of a circular disk. The temperature axis was calibrated by using indium and tin samples supplied by the manufacturer. A typical DSC plot of the tape is shown in Fig. 1.

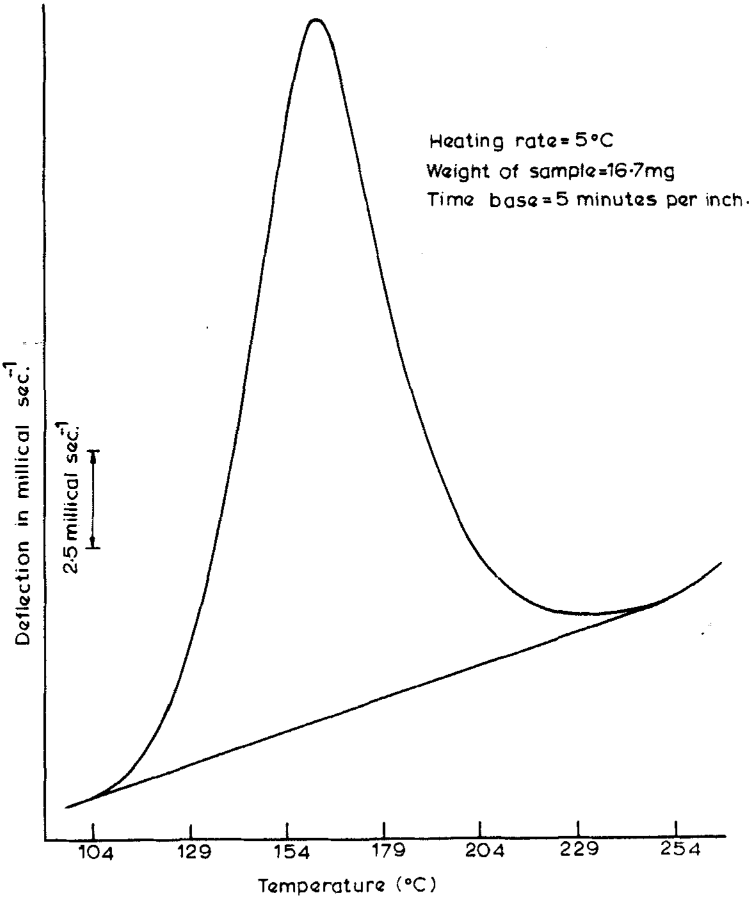


FIG. 1. Dynamic DSC trace of fresh tape.

Accelerated Isothermal Curing Studies

The tapes were isothermally aged at different temperatures (70, 80, 90, and 100° C) in electric ovens maintained isothermally with a fluctuation of ±1° C. The aged samples were taken from each oven at different time intervals, cooled to room temperature, and subjected to DSC runs at 10° C/min scanning.

RESULTS AND DISCUSSION

Kinetics and Mechanism

The method described by Swarin and Wims [1] was used to evaluate the kinetic parameters for the curing process. The rate constant was calculated from

$$k = \frac{A^{n-1} dH/dt}{(A - a)^n} \tag{1}$$

where k is the rate constant which is a function of the temperature T, dH/dt is the height of the DSC curve, A is the total area under the DSC curve, a is the area up to a temperature T, and n is the reaction order. In order to evaluate the value of n for the curing reactions, different values of n, e.g., 0.5, 1.0, 1.5, 2.0 and 2.5, were substituted in Eq. (1) and the k vs T set of data were obtained for each n value and for each heating rate. By using k and T data, the Arrhenius dependence was tested for each n value obtained at all the heating rates. From the least square fit the slope and the intercept were obtained for each set of data for the Arrhenius plot of log k vs 1/T. From this best fit line, log k values were tabulated at each corresponding value of 1/T. The experimental log k values were also put along with each 1/T values. Thus a set of experimental values of log k (A) and calculated values of log k (B) were obtained. The mean deviation in log k for each Arrhenius plot was calculated from

$$\text{Mean deviation} = \sum_{i=1}^{N} \frac{(A_i - B_i)^2}{N} \tag{2}$$

where N is the total number of data points. For a best fit straight line, the mean deviation should have a minimum value [2]. The mean deviations at different n values are presented in Table 1. It can be seen that n = 1.0 and n = 1.5 give the minimum mean deviation. But on the average, n = 1.0 gives a lower value of the mean deviation compared to the mean deviation obtained for n = 1.5. This suggests that the reaction follows first-order kinetics.

In order to further confirm that the reaction is first order, the deviation in the slope and in the intercept both were calculated for the plot of log k vs 1/T. Table 1 further shows that the deviation of the slope and the intercept for n = 1.0 is minimum, suggesting that the reaction follows first-order kinetics. The plots of log k vs 1/T are shown in Figs. 2-5 at different heating rates, and it can be seen that n = 1.0 and n = 1.5 give better straight lines compared to the rest of

TABLE 1. Statistical Data of the Plot of Log KVs 1/T

n	Mean deviation	Slope	Intercept
		a. Heating Rate 2°C/min	
0.5	0.07542	-1623 ± 106	3.1789 ± 0.00030
1.0	0.04310	-3631 ± 84	8.1747 ± 0.00018
1.5	0.02852	-5637 ± 40	13.1600 ± 0.00011
2.0	0.06692	-7769 ± 94	18.4000 ± 0.00027
2.5	0.07884	-9655 ± 111	23.1722 ± 0.00032
		b. Heating Rate 3°C/min	
0.5	0.04228	-2710 ± 87	5.8450 ± 0.00015
1.0	0.03173	-4656 ± 65	10.6160 ± 0.00011
1.5	0.05790	-6616 ± 118	15.4057 ± 0.00021
2.0	0.08744	-8546 ± 179	20.1567 ± 0.00031
2.5	0.12270	-10492 ± 251	24.9263 ± 0.00043
		c. Heating Rate 5°C/min	
0.5	0.04474	-1281 ± 74	2.36500 ± 0.00017
1.0	0.03206	-3137 ± 53	6.80050 ± 0.00012
1.5	0.03659	-5006 ± 61	11.26560 ± 0.00013
2.0	0.05449	-6875 ± 91	15.72000 ± 0.00020
2.5	0.07687	-8744 ± 122	20.19560 ± 0.00028
		d. Heating Rate 10°C/min	
0.5	0.04515	-2634 ± 75	5.28100 ± 0.00016
1.0	0.2823	-4149 ± 47	8.87660 ± 0.00010
1.5	0.03196	-5663 ± 53	12.47020 ± 0.00012
2.0	0.05209	-7177 ± 87	16.06380 ± 0.00017
2.5	0.07665	-8690 ± 127	19.66000 ± 0.00028

the values. In Table 1 the slope corresponding to n = 1 was used to calculate the activation energy (E) which comes out to be around 18 kcal/mol.

The curing of the tape yielded a symmetrical exothermic peak, and it was possible to get accurate peak temperature values at different

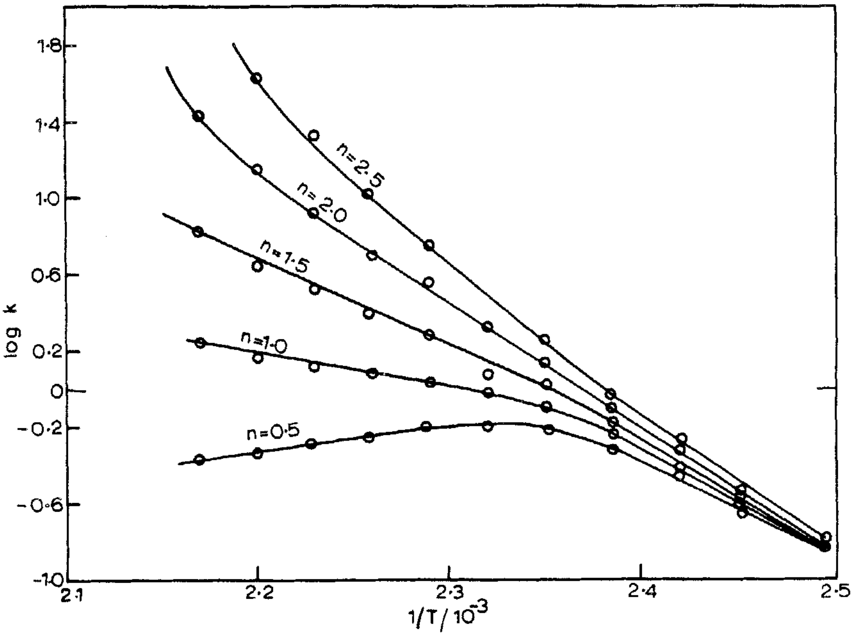


FIG. 2. Plot of log k vs 1/T at a heating rate of 2°C/min.

heating rates (Φ). By adopting Kissinger's method [3] it was possible to calculate the E value from

$$\Phi = BT_m^{\,2} \exp\left(-\frac{E}{R}\frac{1}{T_m}\right) \qquad (3)$$

where Φ is the heating rate in °C/min, T_m is the peak temperature, and B is a constant. The data are presented in Table 2. The value of E was found to be 20 kcal/mol.

The similarity of the E value obtained by Kissinger's method and that obtained by first-order kinetics suggests that 20 kcal/mol should be the authentic value of E for the curing process. In order to compare our E value to that existing in the literature for epoxy curing, reference was made to the study carried out by Oleese and Spetta [4]. They studied the curing kinetics of various epoxy systems: Bisphenol A and epichlorohydrin resin and a solid resin obtained by copolymerization of low molecular weight polyglycol with the above components. The hardener used was amido amine and dicyanadiamide with

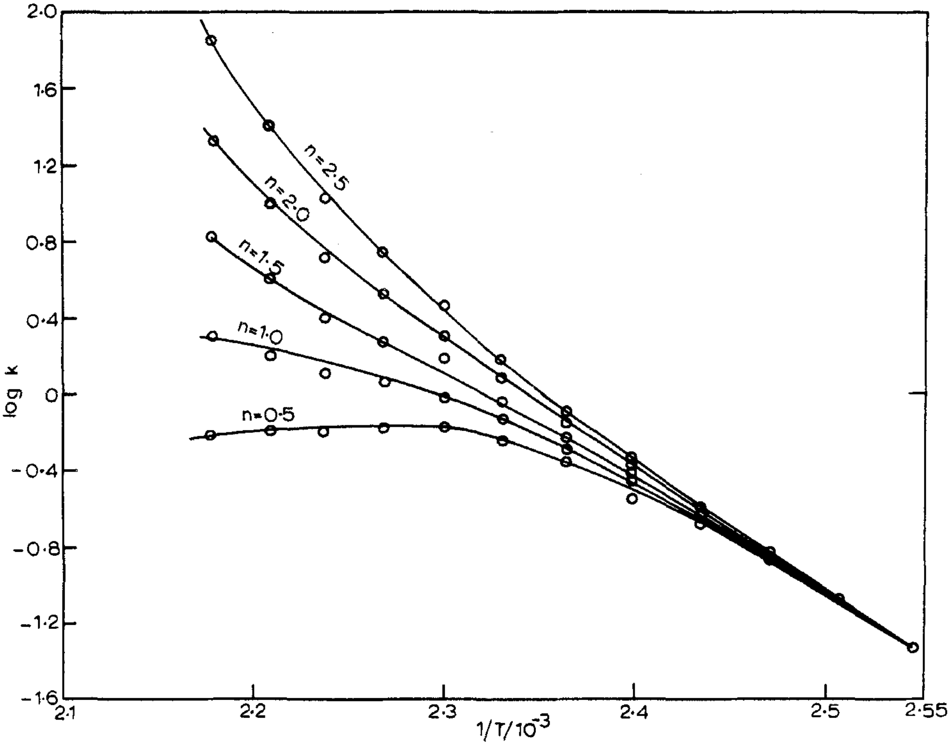


FIG. 3. Plot of log k vs 1/T at a heating rate of 3°C/min.

an accelerator like epoxy amine adduct and an imidazol derivative. They have used various equations to calculate E from the DSC thermograms. They studied the curing kinetics of six different compositions of epoxy hardener-accelerator combinations. Their results are presented in Table 3. It may be seen from Table 3 that most of the E values are around 20 kcal/mol irrespective of the epoxy system and the equations used for calculating the E values. This further supports the belief that the E for curing of an epoxy system may be taken as 20 kcal/mol.

The next step was to understand the significance of the E value. In doing the literature survey it was found that no attempt has been made to understand the meaning of the E value and the associated rate-controlling step. It was thought that the rate-controlling step may be the breakage of the epoxy ring which is the reactive site for cross-linking to occur and perhaps requires the minimum energy for the curing process. The C—O bond energy in the epoxide ring in the polymer is not available and therefore a model compound

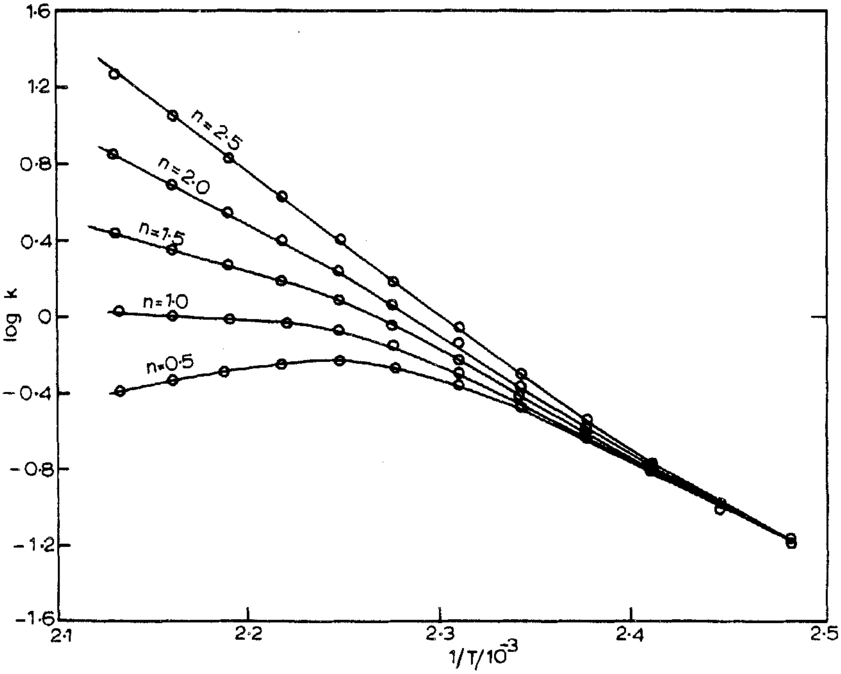


FIG. 4. Plot of log k vs 1/T at a heating rate of 5°C/min.

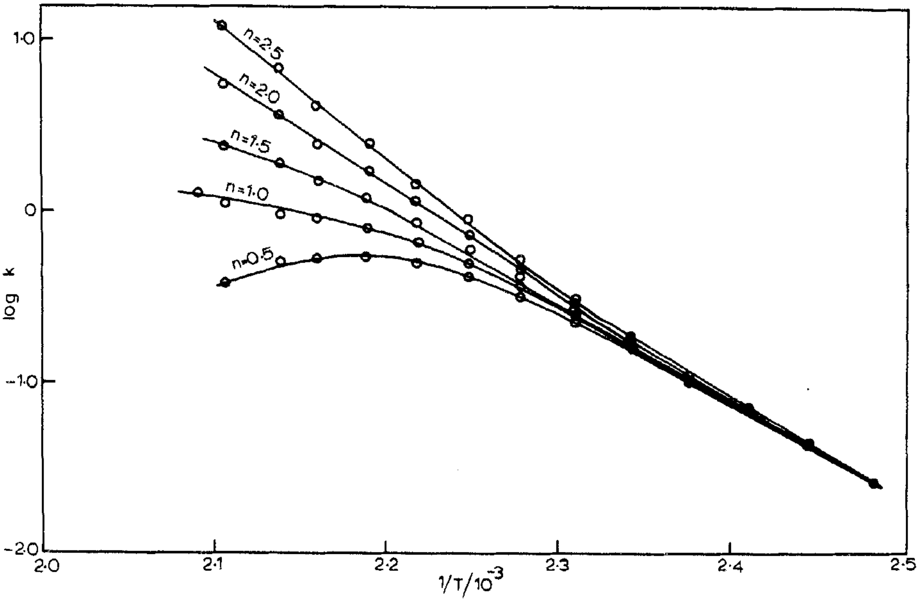


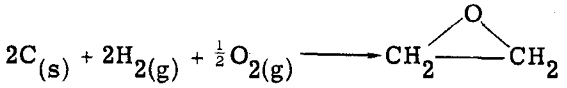
FIG. 5. Plot of log k vs 1/T at a heating rate of 10°C/min.

TABLE 2. Data of the Plot of ln (Φ/T_m^2 vs $1/T_m$) (Kissinger's equation)[a]

No.	Heating rate (Φ) (°C/min)	Peak temperature (T_m) (°K)	$1/T_m$ ($10^{-3}K^{-1}$)	ln (Φ/T_m^2)
1	2.0	326	2.3474	-12.0469
2	3.0	333	2.3095	-11.4157
3	5.0	341	2.3095	-11.0429
4	10.0	353	2.2676	-10.5687
5	20.0	363	2.2075	-9.9292

[a]Correlation coefficient = -0.998
Slope = -9968.68 ± 126.15
Intercept = 12.0335 ± 0.00005
Activation energy = 19.81 ± 0.25 kcal

(ethylene oxide) was chosen to calculate the bond energy associated with the breakage of the epoxide ring. A simple thermochemical calculation was made in the following manner by taking the bond energy values from the literature [5, 6]:

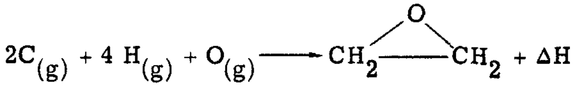


$\Delta H_f = -12.5$ kcal (4)

$H_{2(g)} \longrightarrow 2H_{(g)}$; $\Delta H = 103$ kcal (5)

$C_{(s)} \longrightarrow C_{(g)}$; $\Delta H = 125$ kcal (6)

$O_{2(g)} \longrightarrow 2O_{(g)}$; $\Delta H = 118$ kcal (7)

 (8)

$$\Delta H = 250.0 + 206.0 + 59.0 + 12.5 = 527.5 \text{ kcal} \quad (9)$$

In forming one molecule of ethylene oxide, one C–C, four C–H, and two C–O bonds are formed since one C–C bond energy is 83 kcal and four C–H bond energies are equal to 396 kcal. The remaining energy is utilized in the formation of two C–O bonds. In other words, for

TABLE 3. The Activation Energy Obtained for Epoxy Systems by Various Equations

Epoxy system	Barton[a] (E/kcal mol^{-1})	Rogers-Smith[b] n	Rogers-Smith[b] E/kcal mol^{-1}	Crane et al.[c] n	Crane et al.[c] E/kcal mol^{-1}
A	9.300	1.47	13.760	1.32	22.850
B	15.450	0.36	26.176	0.35	44.707
C	18.820	2.11	20.928	0.94	19.274
D	19.288	2.24	18.787	1.02	19.274
E	14.722	0.52	19.830	0.22	17.883
F	16.350	0.55	20.370	0.24	17.883

[a] Barton's equation:

$$\ln\left(\frac{r_1}{r_2}\right) = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where r_1/r_2 is the ratio of the rates of reaction at the same degree of conversion.

[b] Rogers and Smith's equation:

$$(1 - x)b/b'^2 = (1 - x)BE/bRT^2 - n/\alpha$$

where b is the DSC deflection from base line in millimeters, $b' = db/dt$, is the slope of the DSC curve at any point, x is the fraction reacted, B is the linear heating rate of °C/s, E is the activation energy, R is the gas constant, T is the absolute temperature, n is the reaction order, and α is the total heat of the reaction.

[c] Crane et al.'s equation:

$$(d^2H/dt^2/dH/dT)T^2 = E/R - (nT^2/(1 - x)\Delta H)(dH/dT)$$

where dH/dT is the rate of heat evolution, d^2H/dT^2 is the variation, and x is the fraction reacted up to time t (taken from Ref. 4).

forming two C–O bonds, about 48.5 kcal energy is liberated, suggesting that about 24 kcal energy will be required to break a single C–O bond in ethylene oxide. This value is very near to the E value obtained for the curing process. The difference in the above calculated C–O bond energy and the E for the curing process might be due to the fact that the bond energies in ethylene oxide may be different than the bond energy of the epoxide ring in a macromolecule. The C–O bond energy actually should be lower in a polymer compared to the ethylene oxide. This then confirms that the rate-controlling process is the dissociation of the C–O bond in the epoxide ring leading to the ring opening and subsequent reaction with the amine hardener.

Shelf Life

During aging the tape is slowly cured, thereby resulting in a decrease of the heat evolved for complete curing. The enthalpy loss would therefore measure the aging of the tape during storage. The percentage of curing during aging was measured from the enthalpy data as follows:

$$\% \text{ curing} = \frac{\Delta H_0 - \Delta H}{\Delta H_0} \times 100 \qquad (10)$$

where ΔH_0 is the total heat evolved in the DSC thermogram and ΔH is the heat evolved at a particular time. Plots of the percentage cure as a function of time calculated from Eq. (10) are shown in Fig. 6.

E was calculated from the plot by using the Jacob-Kureishy [7] method and it came out to be 20 kcal/mol. This value is the same as that obtained for the curing of the tape discussed in the earlier section, which suggests that the rate-controlling step during aging is again the slow curing of the resin where the rate-controlling step is the dissociation of the C–O bond of the epoxy resin.

The E value for the aging process was used to calculate the shelf life of the epoxy tape from [8]

$$E = 4.572\,(\log K_2 - \log K_1)\,\frac{T_1 T_2}{T_2 - T_1}$$

where K_1 and K_2 are the reciprocals of the storage period corresponding to any specified change in the tape's property at storage temperatures T_1 and T_2, respectively. The shelf life was calculated

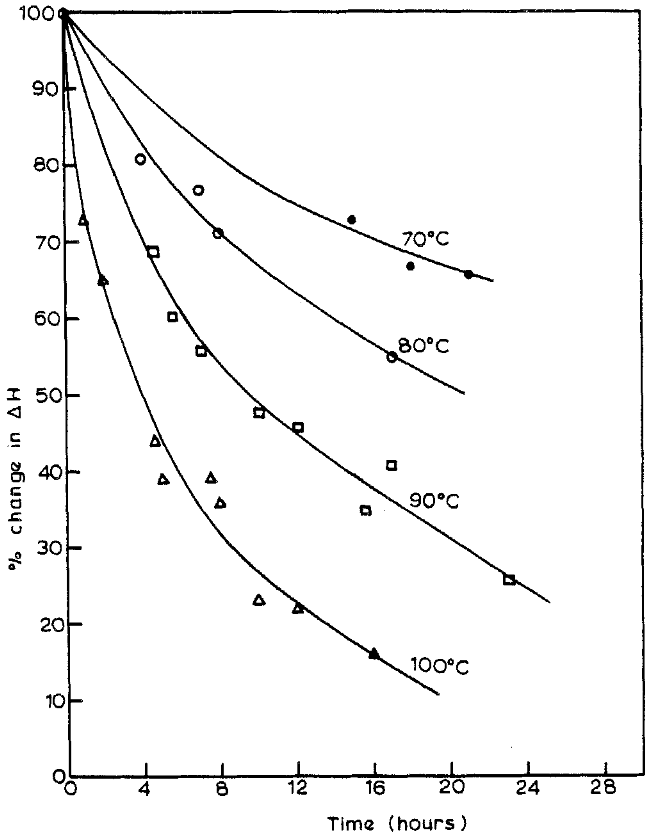


FIG. 6. Plot of percent change in the heat evolved during curing at different temperatures.

TABLE 4. Shelf Life Data of Epoxy Novolac Tape

Extent of curing (%)	Safe useful life (in days) at			
	30°C	25°C	10°C	0°C
10	9 ± 1	16 ± 2	97 ± 9	357 ± 32
20	20 ± 4	35 ± 7	209 ± 45	770 ± 163
30	36 ± 5	63 ± 9	377 ± 54	1388 ± 198
40	59 ± 6	104 ± 10	621 ± 62	2285 ± 230
50	90 ± 7	158 ± 12	947 ± 72	3483 ± 266

at different storage temperatures and for specified extents of curing. The results are presented in Table 4.

REFERENCES

[1] S. J. Swarin and A. M. Wims, "A Method for Determining Reaction Kinetics by Differential Scanning Calorimetry," in Analytical Calorimetry, Vol. 4 (R. S. Porter and J. F. Johnson, eds.), Plenum, New York, 1977, pp. 155-170.

[2] P. D. Lark, B. R. Craven, and R. C. L. Bosworth, The Handling of Chemical Data, Pergamon, London. 1968, pp. 136.

[3] H. E. Kissinger, Anal. Chem., 29, 1702 (1957).

[4] T. Oleese and O. J. Spetta, J. Polym. Sci., Polym. Symp., 53, 113 (1975).

[5] S. Glasstone, Textbook of Physical Chemistry, Macmillan, London, 1962, p. 588.

[6] J. A. Dean, Lange's Handbook of Chemistry, 11th ed., McGraw-Hill, New York, 1973, pp. 3-123.

[7] P. W. M. Jacobs and A. R. T. Kureishy, J. Chem. Soc., Part V, p. 4718 (1964).

[8] K. Kishore and G. Prasad, J. Sci. Ind. Res., p. 414 (1979).

Accepted by editor April 5, 1982
Received for publication May 3, 1982