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STUDY ON CURING OF NOVOLAC EPOXY RESIN
Polyamide hardener systems

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The optimization of proportions of novolac epoxy resin, Dobeckot E4 and polyamide hardener, EH411 has been established by DSC and the data indicates that resin–polyamide, 100:40 and 100:50, appear to be optimum where 'extent of cure' is maximum. The kinetic parameters for these formulations have been evaluated using isothermal and dynamic modes by employing DSC.

The rate constants have been evaluated for curing process of these formulations using isothermal DSC mode in the temperature range of 70°– 90°C. These have also been predicted at 20° ±1°C (room temperature) by extrapolating the data obtained at elevated temperatures. A comparison of the predicted values with the experimental values shows that there is a good agreement between them.

Keywords: epoxy resin, kinetics, polyamide hardener

Introduction

Epoxy resins have been reported for a variety of applications viz. casting, potting, lamination, encapsulation etc. They possess generally high tensile strength but poor elongation. A new generation of epoxy resins i.e. 'Novolac Epoxy Resins' are now being preferred because of their better elongation and retention of their properties at higher temperatures [1].

Novolac epoxy resins have recently been reported for inhibition of composite propellants [2]. These resins are generally in liquid state and are transformed to

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solid state by means of curing agents/hardeners. The inhibition of rocket propellants demands high elongation and sufficient tensile strength [3]. The polyamides are preferred as hardeners/curing agents because the resulting networks are flexible. These polyamides also provide fairly long pot life, good impact strength and excellent adhesion to propellants and they are, therefore regarded as versatile curing agents but their mixing ratios/proportions are not considered as critical as in case of other curing agents/hardeners.

We have recently proposed a method for the prediction of 'State of cure' (SOC) for an unsaturated polyester by the use of differential scanning calorimeter (DSC) [4]. However, the literature survey reveals that no attempt has been made to optimise resin and polyamide proportions and also predict the SOC which indicates attainment of optimum mechanical properties [1, 5]. As the curing process of novolac epoxy resins is exothermic, it was thought of interest to utilise this phenomenon of heat release for monitoring SOC with the help of thermoanalytical technique. In this manuscript, we propose a method for optimisation of proportions of resin and hardener by DSC and prediction of SOC with the help of kinetic parameters.

Materials and methods

Materials

Novolac epoxy resin, Dobeckot E4 and polyamide hardener, EH411 are proprietary products of M/s Dr. Beck & Co., Pune, India. Dobeckot E4 is a cashew nut shell liquid (CNSL) based novolac epoxy resin which is used for inhibition of composite propellants. Various formulations of resin and hardener as 100:X (X varies from 20 to 90 in an increment of 10) were made by adding hardener to resin in required quantity. A batch of 2 g was made for each formulation by mixing resin and hardener thoroughly.

The calorimetric measurements were conducted in the power compensated Perkin-Elmer DSC 7 with 3700 Data Station. The instrument was calibrated using Indium & Zinc metals. About 15–20 mg of sample was taken from the freshly prepared and thoroughly mixed formulation in an aluminium cup, the reference being empty aluminium cup. These cups were heated in a calorimetric cell at 10 deg$\cdot$min^{-1} from 50° to 250°C and total enthalpy was measured for each formulation. Isothermal runs were also carried out on selected formulations viz. 100:40 and 100:50.

Kinetics of curing process for 100:40 and 100:50 formulations were evaluated from dynamic scan by the analysis of a single exotherm.

Mathematical models

The mathematical models used for dynamic technique are:

1) Freeman-Carroll Model [6]

$$\frac{1}{1-n}[1-(1-\alpha)^{1-n}]=Ae^{-(E/RT)}$$

2) Borchardt-Daniel Model [7]

$$\frac{dH}{dt}=k(1-\alpha)^n \quad \text{and} \quad k=Ae^{-(E/RT)}$$

where α = fraction cured
n = order of reaction
θ = Heating rate
T_m = Temperature of peak maximum
E = Activation energy
k = Rate constant

The mathematical models used for isothermal method are

i) Avrami-Erofeev' Model [8–10]

$$-\ln(1-\alpha)^n=kt$$

where t = time.

The residual 'heat of cure' was obtained with dynamic scanning at a heating rate of 10 deg·min^{-1} after each isothermal scan.

The cure kinetics was also followed at room temperature. For this purpose, 10 g batch of formulations 100:40 and 100:50 were prepared and kept at room temperature. Samples from formulations kept at room temperature were withdrawn at different time intervals and 'residual cure' was obtained by scanning sample in dynamic mode with the heating rate of 10 deg·min^{-1}.

Results and Discussion

Novolac epoxy resin alone does not show any exotherm in the temperature range of 50° to 250°C whereas hardener shows only very small exotherm giving only 4 J/g. This indicates that resin does not undergo self-curing in the temperature range studied. On the other hand, various formulations made, show prominent exotherm in the temperature range 50° to 250°C at a heating rate of 10 deg·min^{-1}. DSC scans are given in Fig. 1. It is seen from the Fig. 1 that there is a decrease in the peak maxima with the increase in the proportion of the hardener EH411. This is attributed to the increase in the proportion of hardener which itself shows a small exotherm and initiates reaction at lower temperatures with the increase in the proportion of hardener. The peak area, a measure of cure enthalpy, is given in Table 1. The data shows that the cure enthalpy first increases with the increase in the hardener proportion upto 40 parts i.e. 100:40 formulation and then gradually decreases from 100:50 formulation onwards, being 209.6 and 199.25 $J\cdot g^{-1}$ for 100:40 and 100:50 formulations respectively. This is due to the fact that the extent of reaction increases with the increase in the proportion of the hardener and becomes maximum in 100:40 formulation and subsequently, it shows diluting effect on the overall release of heat as a result of curing of novolac epoxy resin. It is also supported by the data already reported in the literature that these formulations are potential formulations for giving optimum combination of tensile strength and elongation [2].

Table 1 'Heat of cure' of various formulations

No	Formulation		Heat of cure/
	Resin	Hardener	J/g
1.	100	0	–
2.	100	20	138.77
3.	100	30	145.00
4.	100	40	209.60
5.	100	50	199.25
6.	100	60	191.36
7.	100	80	188.20
8.	100	90	132.54
9.	0	100	004.00

Kinetics by 'Freeman-Carroll' and 'Borchardt-Daniel' Models was evaluated in the temperature range of 70°–180°C and 70°–120°C respectively. The best fit is obtained with $n = 0.5$ and the plots for the sam aree straight lines. The activation energy (E) and frequency factor (A) obtained by least square fit are given in Table 2. It is seen from the activation energy data determined by these models that there is a close agreement between E values for 100:40 formulation. Similarly, there is also a good agreement between E values for 100:50 formulation calculated by 'Freeman-Carroll' and 'Borchardt-Daniel' Models.

The temperature range used for isothermal studies is 70°–90°C. The maxima at the zero-time in isothermal run provides the evidence of non-autocatalytic of curing. The α–t curves evaluated from isothermal run for 100:40 formulation is given in Fig. 2. These have been analysed using 'Avrami-Erofeev' Model and the best fit is found to be for $n = 1$. The values of rate constant 'k' evaluated from 'Av-

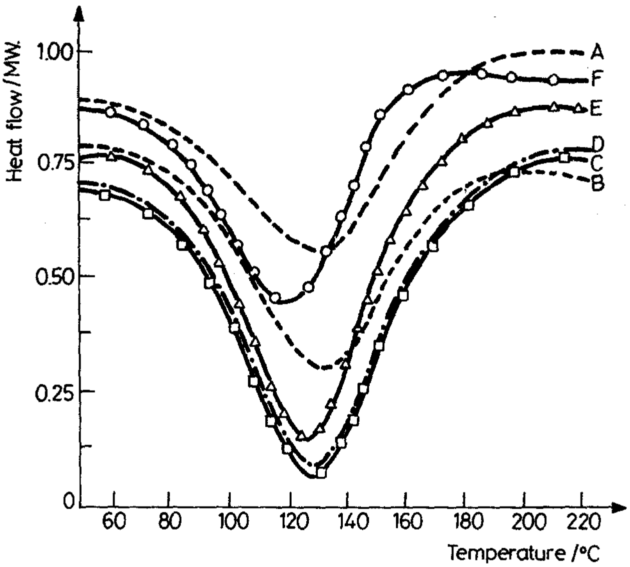

Fig. 1 DSC of various formulations of novolac epoxy resin–polyamide hardener system A – 100:20, B – 100:30, C – 100: 40, D – 100:50, E – 100:60, F – 100:90

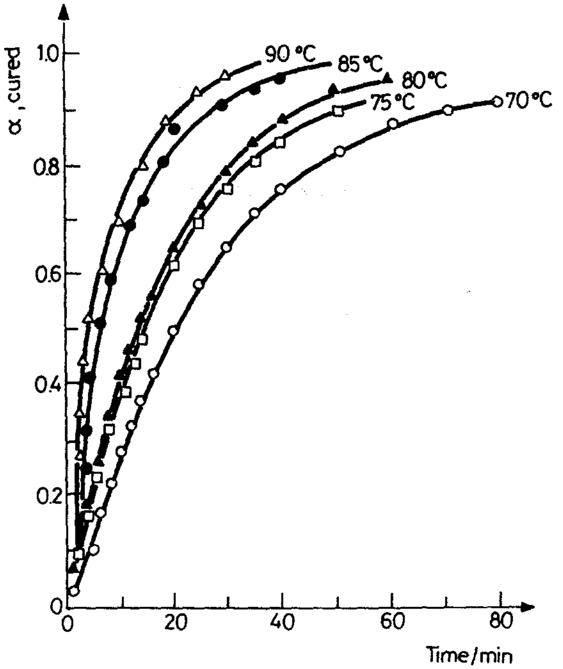

Fig. 2 Plot of $\alpha - t$ for novolac epoxy resin–polyamide hardener system (100:40) at different temperatures

Table 2 Kinetic parameters of novolac epoxy resin–polyamide hardener systems

Mathematical model	Resin:Hardener		Resin:Hardener	
I) Dynamic method	100:40		100:50	
	Activation energy / kJ·mole^{-1}	log *A*	Activation energy / kJ·mole–1	log *A*
1) Freeman-Carroll ($n = 0.5$)	57.85	3.59	50.99	3.14
2) Borchardt-Daniel ($n = 0.5$)	63.87	2.92	55.17	2.43
II) Isothermal Method				
1) Avrami-Erofee'v	43.43	4.09	50.11	4.22

Table 3 Rate constant k at different temperatures (A–E model)

Resin:Hardener

100:40

Temperature / °C	Rate constant / deg·min^{-1}		Time for 99% SOC / h	
	Experimental	Predicted	Experimental	Predicted
70	14.59×10^{-3}	–	2.284	–
75	19.51×10^{-3}	–	1.705	–
80	21.09×10^{-3}	–	1.522	–
85	33.33×10^{-3}	–	1.000	–
90	45.25×10^{-3}	–	0.7366	–
20	4.74×10^{-4}	4.5×10^{-4}	70.18	74.06
30	–	9.819×10^{-4}	–	33.91

Resin:Hardener

100:50

Temperature / °C	Rate constant / deg·min^{-1}		Time for 99% SOC / h	
	Experimental	Predicted	Experimental	Predicted
70	15.0×10^{-3}	–	2.322	–
75	18.4×10^{-3}	–	1.811	–
80	21.4×10^{-3}	–	1.557	–
85	28.8×10^{-3}	–	1.157	–
90	42.8×10^{-3}	–	0.778	–
20	4.638×10^{-4}	4.047×10^{-4}	71.87	83.36
30	–	7.76×10^{-4}	–	42.95

rami-Erofeev' Model at different temperatures are given in Table 3. The kinetic parameters obtained are given in Table 2.

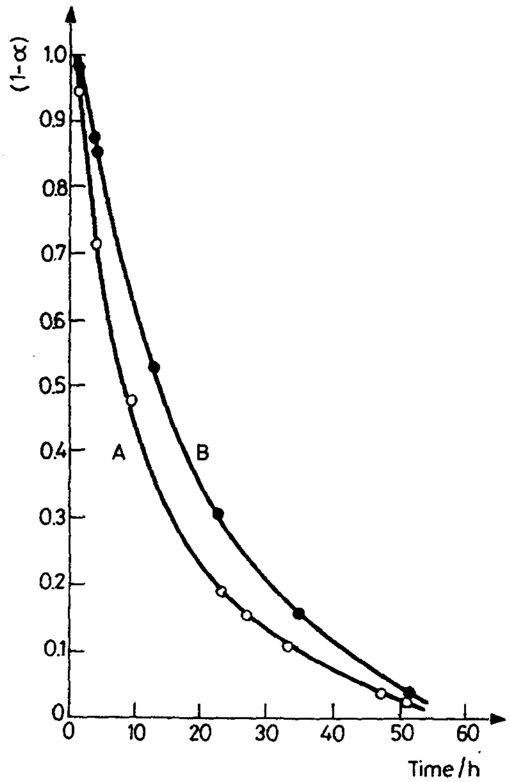

Fig. 3 Plot of residual cure of novolac epoxy resin-polyamide hardener systems
A – 100:40, B – 100:50

The 'kinetics of curing' of Novolac epoxy resin–polyamide EH411 system has also been evaluated at ambient temperature. The plots for 'residual cure' after different time intervals are given in Fig. 3 which shows that the curing of 100:40 formulation is faster as compared to 100:50 formulation.

The rate constants are evaluated by following 'AE Model' for $n = 1$. By employing 'rate constant' data, the time required for achieving 99% SOC was calculated and is given in Table 3. The time is 74 and 82 hrs for 100:40 and 100:50 formulations respectively.

The predicted time to achieve the same order of SOC at different temperatures is also shown in Table 3. The predicted time for 99% cure at 20°C and experimentally calculated time to achieve the same SOC are given in Table 3. It is seen from the data that there is a close agreement between the experimental and predicted values of SOC.

This data is considered very useful in view of the fact that it indicates the time required to achieve maximum SOC, which is considered absolutely essential for attainment of optimum mechanical properties for the formulations. Also, it will prove to be a boon to manufacturers, processors, and users of these systems enabling them to select processing and curing temperature accordingly.

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Zusammenfassung — Mittels DSC wurde die Optimierung des Einsatzverhältnisses von Epoxidnovolackharz Dobeckot E4 und Polyamidhärtungsmittel EH411 durchgeführt. Die Daten ergaben, daß ein Harz-Polyamid-Verhältnis von 100:40 bzw. 100:50 das Optimum zu sein scheint, bei dem die Aushärtung am größten ist. Mittels isothermer und dynamischer DSC-Methoden wurden die kinetischen Parameter für diese Ansätze ermittelt.
Unter Anwendung der isothermen DSC-Methode im Temperaturbereich 70°-90°C wurde die Geschwindigkeitskonstante für den Aushärtungsprozeß dieser Ansätze ermittelt. Diese wurden mittels Extrapolation der erhaltenen Angaben für höhere Temperaturen auch für die Temperatur 201°C (Raumtemperatur) vorhergesagt. Vorhergesagte und experimentell ermittelte Werte stehen in guter Übereinstimmung zueinander.