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CURE REACTION KINETICS OF POLYAMIDE

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ABSTRACT

The kinetic parameters and the heat of polymerisation for the cure reaction of reactive polyamide (made from dimer acid) with epoxide have been established using DSC. The values of energy of activation and pre-exponential factor show a systematic trend with the heat of polymerisation for near-stoichiometric formulations.

INTRODUCTION

Reactive polyamides made from dimer acids have wide applications as thermosetting structural adhesives. The reactive polyamides are usually cured with epoxy resins and the study of the kinetics of the cure reaction is of considerable interest. Differential scanning calorimetry (DSC) is extensively used to study the cure reactions of polymers [1-3] . This communication presents the results of our studies on the kinetics of cure reaction of dimer acid-polyamide with epoxy resin, using DSC.

EXPERIMENTAL

The samples used were: (i) VSSC-developed reactive polyamide made from dimer acid and diethylene tramine (amine content 5-6 equivalents/kg) and (ii) commercial epoxy resin made from bisphenol-A and epichlorohydrine (epoxy content 5-6 equivalents/kg).

The reactive polyamide and the epoxy resin were thoroughly mixed at 10°C (to prevent any initial reaction) in three near-stoichiometric ratios (4:6, 5:5 and 6:4). The samples were taken in aluminium pans of Perkin-Elmer DSC-2C. Heating rate was 10°C min^{-1} and the atmosphere was dry nitrogen purged at a rate of 50 cm^3 min^{-1}. The DSC curves were recorded on a strip chart recorder and the calibration was done using the melting transition

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of pure indium. Computational work was done with CDC computer using FORTRAN IV program.

RESULTS AND DISCUSSION

The DSC curve area was computed using numerical integration techniques (Simpson and Trapezoidal methods) and the difference between the two methods was $\angle 0.5\%$ in all the three cases. Similar observation was made by us earlier [4]. The extent of reaction $\alpha_{(T)}$ was calculated as $A_{(T)}/A_{(f)}$, where $A_{(T)}$ is area under the curve upto temperature T and $A_{(f)}$ is the total area. The kinetic parameters were calculated using Coats-Redfern equation [5].

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} = \frac{AR}{\phi E}\left(1-\frac{2\,RT}{E}\right)e^{-E/RT}$$

(n = order parameter, E = energy of activation,
A = pre-exponential factor, ϕ = heating rate,
R = gas constant and T = temperature °K).

The order parameter, n, was computed by an iteration method described by us earlier [6] and was found to be 1.85. The computed values of the energy of activation and the pre-exponential factor for the three ratios of polyamide and epoxide formulations are given in Table 1.

Table 1. KINETIC PARAMETERS FOR THE POLYAMIDE EPOXIDE CURE REACTION

Formulation No.	Polyamide to epoxy ratio	n	E (kcal mole^{-1})	A (s^{-1})	r	ΔH (cals/gm)
1	4 : 6	1.85	23.33	8.897×10^{10}	0.9995	37.90
2	5 : 5	1.85	24.00	3.104×10^{11}	0.9992	39.45
3	6 : 4	1.85	26.32	1.134×10^{13}	0.9990	44.89

The reaction is exothermic and the heat of reaction was computed from the DSC peak area of the three mixtures in comparison with that of the standard (melting transition of indium). The ΔH values are also given in Table 1.

CONCLUSIONS

(i) The correlation coefficients, r, for the kinetic curves are near unity indicating perfect fits.

(ii) The best fit values of 'n' show that the reaction is second order.

(iii) The kinetic parameters are in the range of: $E = 23 - 26$ kcal mole^{-1} and $A = 10^{10} - 10^{13}$ sec^{-1}. The values of E and A are not much different for the formulations 1 and 2. They show an increase for the formulation 3.

(iv) The heat of polymerisation also show a similar trend. The ΔH values for the formulations 1 and 2 are 37.90 and 39.45 cals/gm respectively, while for the formulation 3, it shows an increase to 44.89 cals/gm.

(v) This type of correlation between heat of reaction and energy of activation has been reported earlier for some endothermic decomposition reactions [7]. In this case, E and log A are linearly related showing the kinetic compensation effect [8]. Heat of polymerisation is, therefore, related to both E and A.

(vi) The constancy of the values (E, A and ΔH) for the formulations 1 and 2 shows that the stoichiometry is attained in this range. Arriving at the stoichiometry of the polymer cure reaction is of importance, because of a number of possible side reactions.

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