Asian Journal of Chemistry Vol. 16, No. 2 (2004), 744–750

Kinetic Studies of Curing Reaction of Epoxy Resins

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The kinetic study of epoxy resins, using triethanolamine (TEA) as catalyst having different concentrations, were carried out for the various systems, *viz.*, diglycidyl ether of bisphenol-A (DGEBA), epoxidized 2,4-dichlorophenol-1,2-dichlororoethane oligomer (EBPE) and phthalic anhydride (PA) as curing agent [1:1:2] the extent of reaction (P) was studied for above said systems at elevated temperature. Certain reactions for cure of epoxy resins were carried out with and without amine accelerator.

Key Words: Kinetic, Epoxy resins.

INTRODUCTION

The epoxy resins are one of the most versatile of the modern plastics. The thermosetting epoxy groups possess a number of unusually valuable properties immediately amenable to use in the formation of adhesives, sealing liquids, cold solders, coatings, laminates and coatings. Phthalic anhydride as it has become an inexpensive commodity for chemical resin synthesis, used as a hardner in presentepoxy curing reactions[1–4]. Dearborn *et al.*[2, 5] reported the curing of various epoxy resins with PA, in presence and in absence of amine accelerators and reported highest cross-linking in amine catalyzed anhydride-epoxide resins. The probable mechanism was reported in detail in investigation of reactions between epoxide and anhydride in presence of amines[6]. Shear modulus, torsion oscillation, shrinkage and aging properties were discussed during the curing reaction of modified epoxy resins in presence of PA[7]. The Span patent[8] reported the resins having varied flexibility and hardness as well as their use in preparing varnishes, enamels, adhesives from curing reaction of epoxidized resins and phthalic anhydride in presence of various amines. The reportings[1–8] of curing reaction of epoxy resins exhibited wide applicability and thus made us explore further in this field. The present paper reports the kinetic study of DGEBA and EBPE with PA in different systems in presence of triethanolamine with various concentrations.

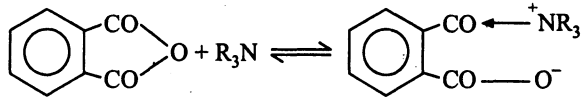
EXPERIMENTAL

The required epoxy resins DGEBA and EBPE were prepared by reported method[9, 10]. The dry methanol and pyridine required for purification of PA was obtained in pure form by the process in literature[11]. All other chemicals used were of analytical grade.

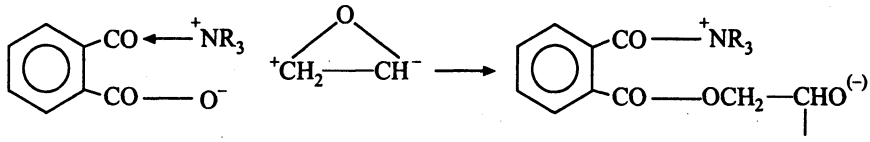
Kinetic reaction

In a test tube 6" × 1" DGEBA, EBPE and PA were taken in molar proportion [1 : 1 : 2]. In each tube a thermometer was placed and curing was carried out at 80°C adding known quantity of TEA as catalyst. The stopwatch was started immediately after the addition of amine. The results were are recorded in Tables 2, 3 and reaction mechanism are described in Scheme-1.

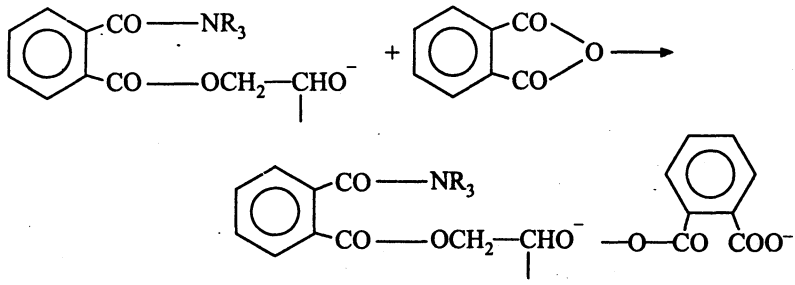
(1) Activation of anhydride by amine



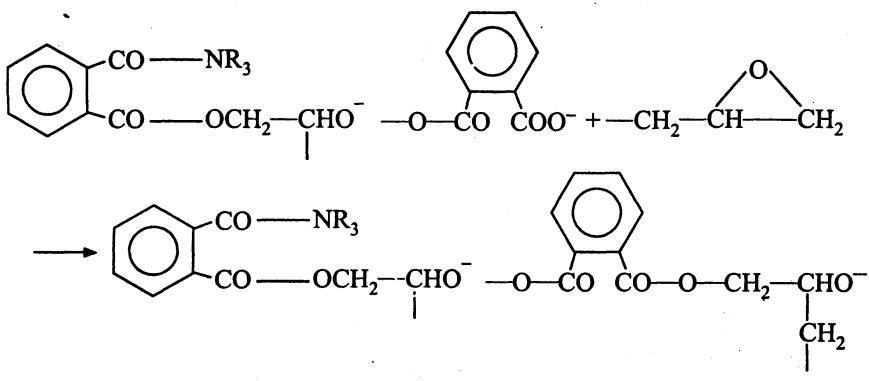
(2) Cooboxyl ion reacts with epoxide group of DGEBA



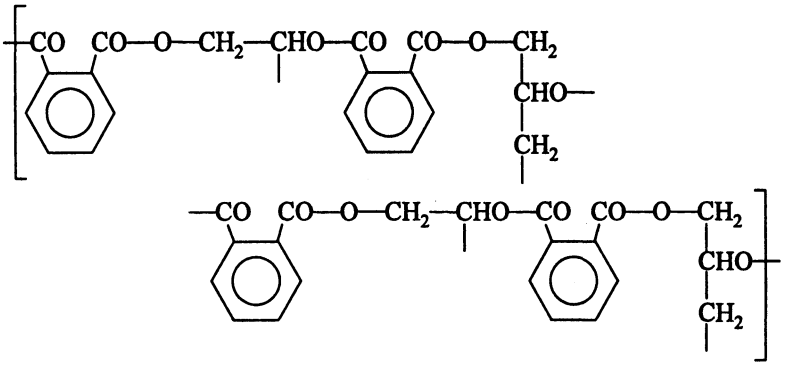
(3) Alkoxid ion reacts with anhydride



(4) Carboxyl ion reacts with epoxide group of EBPE



(5) The displacement of the amine by alkoxide ion would continue the formation of polyester.



Scheme-1

The specifications of DGEBA and EBPE epoxy resins were determined by standard methods. Number average molecular weights ($\overline{M}_n$) for DGEBA and EBPE were 342 and 508 determined by vapour pressure osmometer (VPO) respectively. Intrinsic viscosities [η] for DGEBA and EBPE were 3.1 and 2.8 dL g^{-1} were measured in carbon tetrachloride at 30°C respectively. The percentage purity of phthalic anhydride (97.1%) as well as the epoxy equivalent weight for DGEBA (195 g/equiv.) and for EBPE (405 g/equiv.) were determined by the methods described in literature[11, 12].

RESULTS AND DISCUSSION

The specifications of epoxy resins DGEBA and EBPE were acertained from the various experimental methods. The method of esterification[12] was used for the determination of anhydride content of epoxy resins. To measure the extent of reaction (P) either epoxide or anhydride content of the sample could be determined. But the determination of epoxide content gives comparatively more errors than that determined by anhydride content[13]. Hence the method of anhydride content was preferred in the present work. The detailed results and reaction conditions are given in Tables 1 and 2, and plots are given in Figs. 1–6.

TABLE-1
EFFECT OF TEMPERATURE (AFTER 120 min) ON P AND K FOR THE SYSTEM DGEBA + EBPE + PA [1 : 1 : 2] USING 1% TEA

Temperature (°C)	Gel time	PET (°C)	P	K
130	15.0	148	0.710	0.0339
140	11.0	152	0.889	0.0700
150	4.0	160	0.972	0.1727

Effect of temperature: It is revealed that as reaction temperature increased the gel time decreased but peak exotherm temperature, extent of reaction and reaction rate increased. About 80–90 % of reactants were consumed up to gel time, that is most of the reaction was completed before gelation and became very

slow after gelation. The results are given in Table-1 and plots are shown in Figs 1 and 2.

TABLE-2
EFFECT OF CATALYST (TRIETHYLAMINE - TEA) CONCENTRATION ON P AND K (AFTER 120 MIN) FOR THE VARIOUS SYSTEMS AT 135°C

Systems	TEA (%)	Gel Time (min)	PET (°C)	P	K
DGEBA + EBPE + PA (1 : 1 : 2)	–	70.0	136	0.535	0.0069
	0.5	14.0	145	0.825	0.0262
	1.0	9.0	151	0.890	0.0601
	2.0	7.3	153	0.931	0.0984
DGEBA + PA (1 : 1 : 2)	–	50.0	138	0.683	0.0237
	0.5	2.0	180	0.935	0.1120
EBPE + PA (1 : 1 : 2)	1.0	3.0	180	0.868	0.0610
	2.0	2.0	180	0.931	0.1030

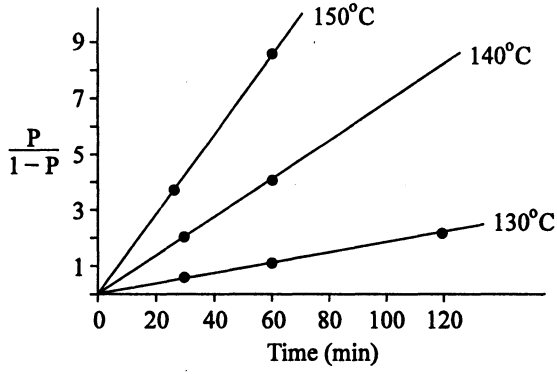


Fig. 2

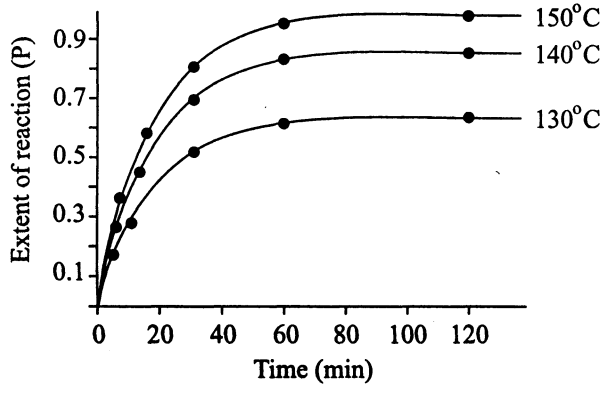


Fig. 2

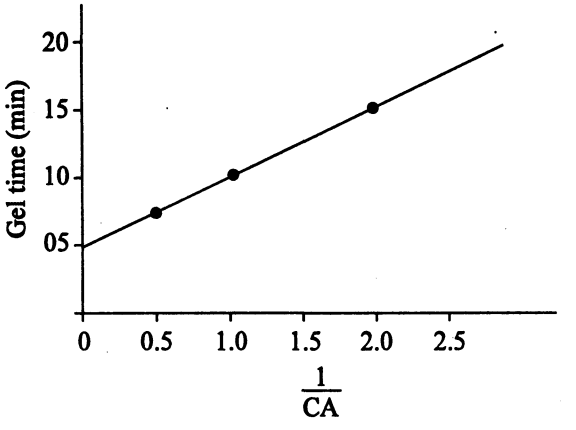


Fig. 3

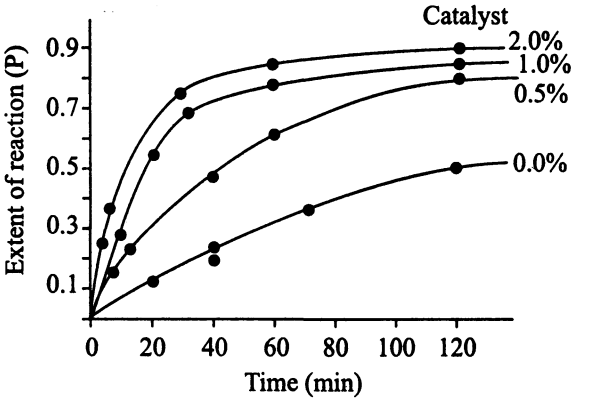


Fig. 4

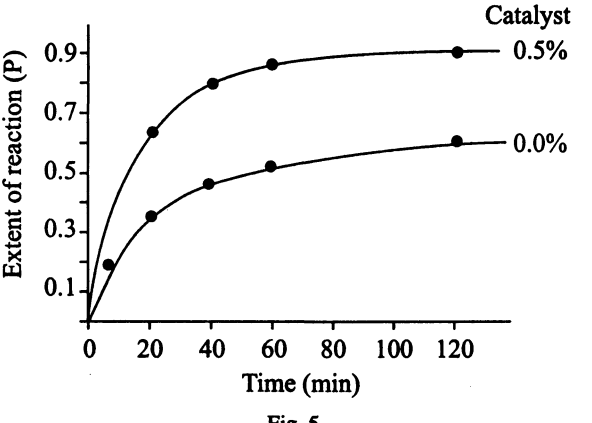


Fig. 5

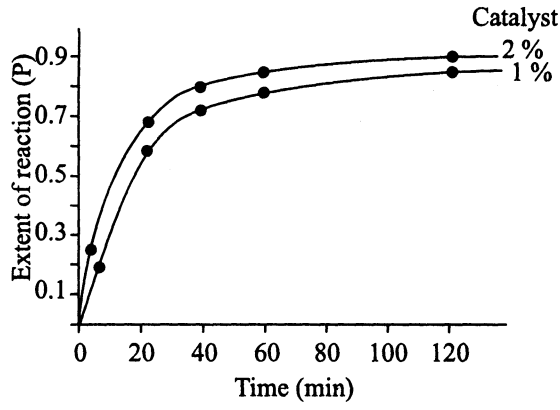


Fig. 6

Effect of concentration of catalyst: It has been found that the rate of reaction of DGEBA, EBPE with PA [1 : 1 : 2] was sluggish in the absence of catalyst as it took 70 min for gel formation and P was only 0.535 after 70 min. But the addition of the catalyst in small quantity largely activated the reaction rate, extent of reaction and PET. The results are given in Table-2 (Fig. 4). The relation between the gel time of epoxy resin to the reciprocal concentration of the catalyst (Fig. 3), shows that gel time is inversely proportional to the catalyst concentration.

The reaction between equimolar DGEBA and PA in absence of catalyst was found to be very slow showing gel time 50 min. and P 0.683. But after 120 min. only 0.5% catalyst was sufficient to catalyze the reaction to 0.935P in 120 min. The K-values for this system with and without catalysts, 0.1120 and 0.0237, also agree with these observations. The results are presented in Table-2 (Fig. 5).

The reaction between equimolar EBPE and PA without catalyst did not complete even after 120 min. Hence to find out the effect of catalyst concentration on this system, two different concentrations, 1% and 2%, of triethanolamine were used. The extent of reaction for 1% catalyst was 0.868 and that for 2% catalyst was 0.931. The results are given in Table-2 (Fig. 6).

Thus, The present study on the epoxy-resins revealed that whatever might be the type of the epoxy system, it requires a small amount of catalyst for the completion of the reaction within a reasonable time period. Increase in the catalyst concentration has marked effect on gel time, peak exotherm temperature, extent of reaction and hardening rate for all types of epoxy-resin systems for curing reaction.

Conclusion

1. As temprature increases gel time decreases and peak exotherm temperature increases in the given curing reaction of epoxy resins.
2. As concentration of catalyst TEA increases, P and K of the curing reaction increase.
3. A small amount of catalyst is required for the completion of curing reaction within reasonable time period.

ACKNOWLEDGEMENT

The author is thankful to CSIR New Delhi for financial assistance.

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(*Received*: 14 June 2003; *Accepted*: 04 December 2003) AJC-3261