Curing kinetics of epoxy resin using quaternary ammonium guar gums as catalyst

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Abstract

Various quaternary ammonium compounds of guar gum (QAGG) have been synthesised and used as catalysts for curing reactions of epoxy resin. The detailed kinetics of the curing reactions of the system diglycidyl ether of bis-phenol A (DGEBA)/phthalic anhydride (PA) have been studied using a selected catalyst.

**Key words:** Epoxy resin, curing kinetics.

1. Introduction

Several workers[1-3] have studied the curing of epoxy resins with acid anhydrides both in the presence and absence of a catalyst. Tanaka and Kokiuchi[4,5] have made a systematic study of the kinetics and the reaction mechanism involved in the epoxide-anhydride reaction. The effect of amines and other compounds having active hydrogen such as acid, alcohol and phenol as catalyst on the curing reaction has also been studied. The amines, widely used as curing agents for epoxy resins, are toxic in nature. Hence, recently amine adducts or quaternary salts have gained importance as curing agents[6,7].

In the present investigation, the curing of diglycidyl ether of bisphenol A (DGEBA)/phthalic anhydride (PA) has been studied kinetically in the presence of quaternary ammonium compounds of guar gum (QAGG) as catalysts. The effect of temperature and concentration of catalyst on the curing reaction has also been studied.

2. Experimental procedure

Liquid epoxy resin DGEBA was prepared following a method described by Sorenson and Campbell[8]. Epoxy-equivalent weight (EE), determined by the hydrochlorination method[9], was found to be 192 g/eq. Reagent-grade phthalic anhydride was purified before use. QAGG samples were prepared by treating guar gum with condensation product of epichlorohydrin and tertiary amines, either heterocyclic or aliphatic[10] (Scheme I).

(a) Epichlorohydrin

(b)
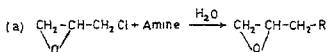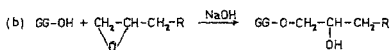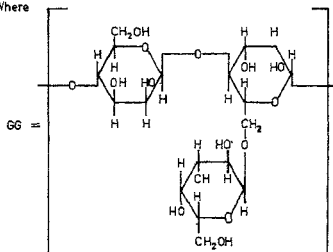
Where GG = Guar Gum

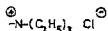Designation for QAGG sample

R =

Pyridinium chloride — A

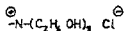2,6-Diamino pyridinium chloride — B

Quinolinium Chloride — C

Triethyl ammonium Chloride — D

Triethanol ammonium Chloride — E

SCHEME I.

2.1. *Curing kinetics*

PA and DGEBA (mole ratio 1:1) were weighed in a $6'' \times 1''$ test tube and heated in a thermostated oil bath. After mixing a catalyst thoroughly with the above mixture, the sample was withdrawn and used as control. The reaction mixture in the test tube was kept stirring during heating. Aliquots of the reaction mixture were taken out at convenient time intervals. When gelation commenced, there was a sudden rise in the temperature of the reaction mixture. The highest temperature obtained was recorded and taken to be the peak exotherm temperature of the reaction.

After gelation, heating was continued for a particular time period (120 min). The test tube was taken out from the oil bath, cooled and the glass was carefully cracked and peeled off from the specimen. A part of the solid resin was ground to fine powder and was analysed for anhydride content.

The anhydride contents of aliquots from the reaction system were determined by esterification method[11]. A known amount of reaction mixture was analysed to determine the anhydride content by dissolving it in methanol-water (1:1) and methanol-pyridine (1:1) mixtures for estimating the total acidity (b), and acid content (a), respectively, using standard alkali as titrant. The anhydride content was then calculated using the following equations:

$$\% \text{Anhydride} = \frac{(b-a) \times 148 \times 100}{1000}. \tag{1}$$

The extent of reaction p was determined using equation (2)

$$p = \frac{(C_i - C_t)}{C_i} = 1 - \frac{C_t}{C_i} \tag{2}$$

where C_t and C_i are the concentrations of the anhydride in the reaction system at the time of measurement and at the initial time of the reactions, respectively. The rate of second-order reaction, k_2, was obtained from

$$\frac{p}{(1-p)} = k_2 C_i t = k_2' \cdot t \tag{3}$$

when the initial concentration of the epoxide C_i was the same as that of phthalic anhydride.

2.2. *Gel fraction*

Cured epoxy resin (1 g) was extracted with tetrahydrofuran for 72 h using soxhlet apparatus. The insoluble part was collected and dried under vacuum until no weight change was detected. The gel fraction was calculated as

$$\text{Gel fraction} = \frac{\text{Weight of insoluble material}}{\text{Weight of initial material}}.$$

2.3. *Solubility parameter by intrinsic viscosity method*

Solubility parameters were determined by estimating intrinsic viscosity $[\eta]$ of the samples before gelation[12]. The intrinsic viscosities of samples in dimethyl formamide (DMF),

Table I
Solubility parameter and molar volume of solvents

Solvent	Solubility parameter $\delta \, (\text{cal/cc})^{1/2}$	Molar volume V (cc)
DMF	12.1	77
Butanol	11.4	81
Dioxane	10.0	86
Chloroform	9.3	81

butanol, dioxane and chloroform were estimated by the usual extrapolation method[13]. The values of solubility parameter (δ) and molar volume (V) of solvents are represented in Table I.

3. Results and discussion

The catalytic activity of various amines, their QAGG samples and guar gum itself on the gel time and peak exotherm temperature of the system DGEBA/PA were evaluated at 1% level (Table II).

The gel time of the system DGEBA/PA in the presence of guar gum was found to decrease from 62 to 36 min. This may be attributed to free hydroxyl groups present in guar gum molecules. Even though guar gum reduces the gel time, it did not seem to be a suitable catalyst because of its very long pot life. Hence modification of guar gum by quaternization

Table II
Effect of different catalysts on the gel time and peak exotherm temperature in the system DGEPA/PA

System: DGEBA (10 g), PA (4.5 g), Catalyst 1%, Temp. (140°C)

Catalyst	Gel time (min sec)		Peak exo-therm temp. (°C)	Catalyst*	Gel time (min sec)		Peak exotherm temp. (°C)
—	62	32	143	—	—	—	—
Guar gum	36	25	142	—	—	—	—
Pyridine	00	32	20	A	11	00	168
2,6-Diamino pyridine	02	32	174	B	12	45	147
Quinoline	00	47	196	C	10	50	152
Triethyl amine	02	45	182	D	10	45	150
Triethanol amine	03	47	160	E	11	20	150

*Catalysts used were quaternary ammonium guar gums.

was thought of. The gel time in the presence of QAGG samples and pure amines varied from 10 to 13 min and 0.5 to 4 min, respectively. This shows that QAGG samples functioned as mild catalysts compared to toxic amines, but QAGG may be more useful in large castings as they are non-toxic, non-volatile and have comparatively long pot life and low peak exotherm temperature.

3.1. *Effect of temperature on the curing reactions*

To study the effect of temperature on the curing reactions, three different temperature (*i.e.*, 130, 140 and 150°C) were selected. Figure 1 shows the effect of temperature on the curing reaction of the system DGEBA/PA with 1% of (2-hydroxy-3-triethanol ammonium chloride) propyl guar gum ether (E) in Scheme I, as catalyst.

For the said system, with an increase in reaction temperature, the gel time decreased while the peak exotherm temperature and the extent of reaction increased. Up to the gel time, 80–90% of the reactants were found to be consumed in all cases. Thus a major part of the reaction was completed before gel time, and the reaction became quite slow after gelation. After 120 min, the extent of reaction was 0.90, 0.92 and 0.97 at the reaction temperatures 130, 140 and 150°C, respectively.

The data represented in fig. 2 show that the curing reaction followed second-order kinetics up to about 80% conversion.

3.2. *Effect of catalyst concentration on the curing reaction*

The effect of catalyst (E) concentration on the curing reaction of the system DGEBA/PA at 140°C is shown in fig. 3. It was found that the curing reaction of the system was very
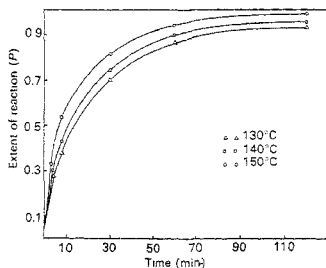

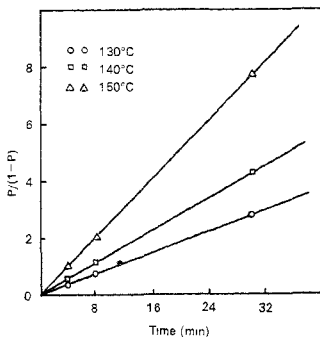FIG. 1. Effect of temperature on the reaction of DGEBA/PA system with 1% E as catalyst.

FIG. 2. Plots of time *vs* $P/(1-P)$: Reaction of DGEBA/PA with 1% E as catalyst.
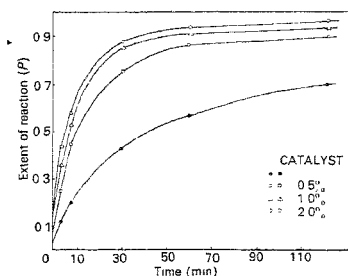
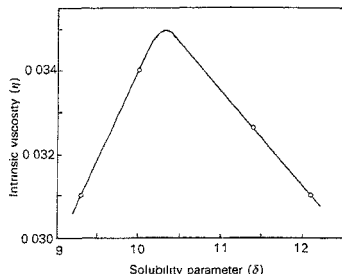FIG. 3. Effect of E as catalyst on the reaction of DGEBA/PA at $140 \pm 1°C$.

FIG. 4. Plot of solubility parameter of solvent (δ) *vs* intrinsic viscosity. Computation of $[\eta]_{max}$ for the system DGEBA/PA at 130°C (sample withdrawn time = 0 min.)

sluggish in the absence of a catalyst. It took about 60 min to gel even though it did not harden sufficiently. The extent of reaction after 120 min was found to be only 0.69, while it was found to be 0.89, 0.92 and 0.96 in the presence of 0.5, 1.0 and 2.0% E as catalyst, respectively. It was also observed that with increase in concentration of the catalyst, the gel time decreased, while the extent of reaction and peak exotherm temperature increased.

Table III
Effect of temperature and catalyst (E) concentration on intrinsic viscosity and solubility parameter of the system DGEBA/PA

Temp. (°C)	Catalyst concen- tration (%)	Sample withdrawn time (min)	dl g^{-1}				$[\eta]_{max}$	Solubility parameter (δ_p)
			DMF	Butanol	Dioxane	Chloroform		
140	—	0	0.031	0.032	0.034	0.031	0.035	8.1
		4	0.038	0.041	0.043	0.037	0.045	8.5
		8	0.103	0.109	0.117	0.102	0.119	9.1
140	0.5	0	0.031	0.032	0.034	0.031	0.035	8.1
		4	0.039	0.042	0.045	0.038	0.046	8.5
		8	0.119	0.125	0.133	0.118	0.135	9.1
140	1.0	0	0.031	0.032	0.034	0.031	0.035	8.1
		4	0.040	0.042	0.045	0.039	0.046	8.6
		8	0.122	0.130	0.139	0.121	0.141	9.2
140	2.0	0	0.031	0.032	0.034	0.031	0.035	8.1
		4	0.050	0.056	0.060	0.050	0.062	8.7
		8	0.155	0.165	0.183	0.154	0.184	9.5
130	1.0	0	0.031	0.032	0.034	0.031	0.035	8.1
		4	0.037	0.039	0.042	0.036	0.043	8.5
		8	0.085	0.090	0.096	0.084	0.098	8.9
150	1.0	0	0.031	0.032	0.034	0.031	0.035	8.1
		4	0.061	0.064	0.069	0.060	0.071	8.7

Table IV
Effect of temperature and catalyst (E) concentration on gel fraction of the cured samples of the system DGEBA/PA after 120 min

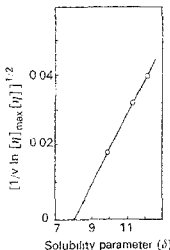| Temp. (°C)	Catalyst conc. (%)	Gel fraction (%)
140	—	81.22
140	0.5	81.56
140	1.0	86.27
140	2.0	90.50
130	1.0	82.19
150	1.0	90.63

FIG 5. Plot of solubility parameter of solvent (δ) vs $[1/V \ln([\eta]_{max}/[\eta])]^{1/2}$. Computation of solubility parameter for the system DGEBA/PA (i.e., δ_p) at 130°C (sample withdrawn time = 0 min.)
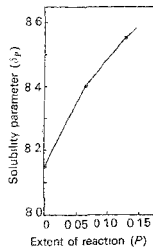
FIG. 6. Plot of extent of reaction (p) vs solubility parameter of sample (δ_p).

3.3. *Effect of temperature and catalyst on solubility parameter and gel fraction*

The intrinsic viscosity $[\eta]$ in different solvents (Table III) was plotted against solubility parameter (δ) of the respective solvents (fig. 4). The $[\eta]_{max}$ was estimated from fig. 4 and used to calculate the values[12] of $[(1/V) \ln([\eta]_{max}/[\eta])]^{1/2}$ which were then plotted against δ (fig. 5). The solubility parameter (δ_p) of samples obtained from the intercept of fig. 5 is recorded in Table III. Data of Table III and fig. 6 reveal that the solubility parameter of sample increases with increasing extent of reaction and reaction time which might be due to the subsequent increase in cross-link density. It is also affected by temperature and catalyst concentration and would be maximum just before complete cross-linking.

Gel fraction value (Table IV) also increases with increase in temperature and catalyst concentration indicating that cross-linking of epoxy resin has increased.

4. Conclusion

Even though QAGG samples function as mild catalysts they are preferred for the curing reaction of epoxy resins, because of their non-toxic and non-volatile nature and long pot life. The gel time, peak exotherm temperature, extent of reaction, gel fraction and solubility parameter are affected by catalyst concentration and temperature of the curing reaction.

Acknowledgements

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