

## Thermal analysis of epoxy curing using polyfunctional active esters as curing agents <sup>α</sup>

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### Abstract

The curing behavior of bisphenol A diglycidyl ether (BADGE) has been studied by differential scanning calorimetry and IR spectroscopy using active esters, the trifunctional compound 1,3,5-triacetoxybenzene (TAB) and tetrafunctional tetraphenoxycarbonyl pentaerythritol (TPCP) as curing agents, with which no free hydroxyl groups are left in the cured resins. The effects of the ratio of ester groups to epoxide groups ( $r$ ) in the reaction mixture on the glass transition temperature ( $T_g$ ) and the thermal stability of the cured resins were also examined by thermomechanical analysis and thermogravimetry respectively. The  $T_g$  has the maximum value of 72°C at  $r=1$  for either TAB or TCP as curing agent. The thermal stability increases with increasing value of  $r$ .

### INTRODUCTION

Epoxy resins are usually cured with polyfunctional amines, alcohols and carboxylic acids. However, the reaction of epoxide groups with amino, hydroxyl and carboxyl groups can form hydroxyl groups. Consequently, epoxy resins cured with these conventional curing agents have pendant hydroxyl groups, which impair the electrical and lipophilic properties of the cured resins. Recently, it has been found that polyfunctional active esters with three or more ester groups are effective for epoxy curing when quaternary ammonium salts or crown ether–salt complexes are used as catalysts, and leave no free hydroxyl groups in the cured resins [1].

Our aims here were to examine the curing behavior of bisphenol A diglycidyl ether (BADGE) using the trifunctional compound 1,3,5-triacetoxybenzene (TAB) and tetrafunctional tetraphenoxycarbonyl pentaerythritol (TPCP) as polyfunctional active esters and tetrabutylammonium

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bromide (TBAB) as catalyst by differential scanning calorimetry (DSC) and IR spectroscopy and to clarify the effects of the concentrations of curing agent and catalyst and of reaction temperature on epoxy curing with these curing agents. The glass transition temperature ( $T_g$ ) and thermal stability of the cured resins were also determined by thermomechanical analysis (TMA) and thermogravimetric analysis (TG) respectively.

## EXPERIMENTAL

Epikote 828 (epoxy equivalent, 205) was used as received as the bisphenol A diglycidyl ether (BADGE). Reagent grade tetrabutylammonium bromide (TBAB) was used without further purification. 1,3,5-Triacetoxybenzene (TAB) was prepared by reacting 1,3,5-trihydroxybenzene with acetic anhydride using pyridine as catalyst [2], and tetraphenoxycarbonyl pentaerythritol (TPCP) was obtained from phenyl chloroformate and pentaerythritol [3].

A Perkin–Elmer DSC System 4 was used to follow the curing process and to determine the heat of curing. The DSC measurements were carried out using 5–10 mg of the curing mixture. IR spectra of the curing mixture on a KRS plate were recorded with a JASCO IR-810 to follow the isothermal curing reaction. TMA (penetration mode) was carried out with a Rigaku Denki Thermoflex thermal analyzer to determine the glass transition temperature of the cured resins. The thermal stability of the cured resins was examined with a Rigaku Denki Thermoflex TG thermal analyzer in a nitrogen atmosphere.

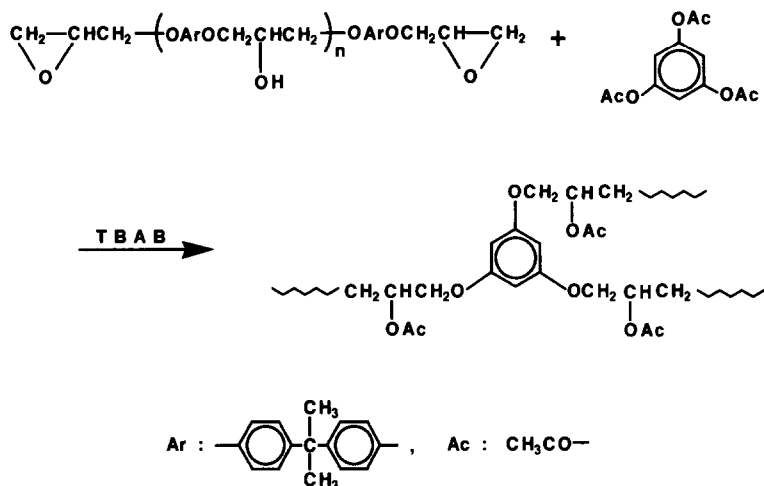
## RESULTS AND DISCUSSION

The reactions of bisphenol A diglycidyl ether with 1,3,5-triacetoxybenzene and tetraphenoxycarbonyl pentaerythritol are shown in Schemes 1 and 2, respectively; no free hydroxy groups are left after either reaction.

### *Curing with 1,3,5-triacetoxybenzene (TAB)*

The isothermal curing reactions were carried out at 70, 90, 110 and 130 °C on a mixture (1 : 1 by equivalents) of BADGE and TAB as curing agent using 2.5 mol.% of TBAB as catalyst. The progress of reaction was followed by determining the extent of reaction of epoxide groups from the ratio of the absorbance of the band due to oxirane rings (910  $\text{cm}^{-1}$ ) to that due to benzene rings (1600  $\text{cm}^{-1}$ ) in the IR spectra (see Fig. 1).

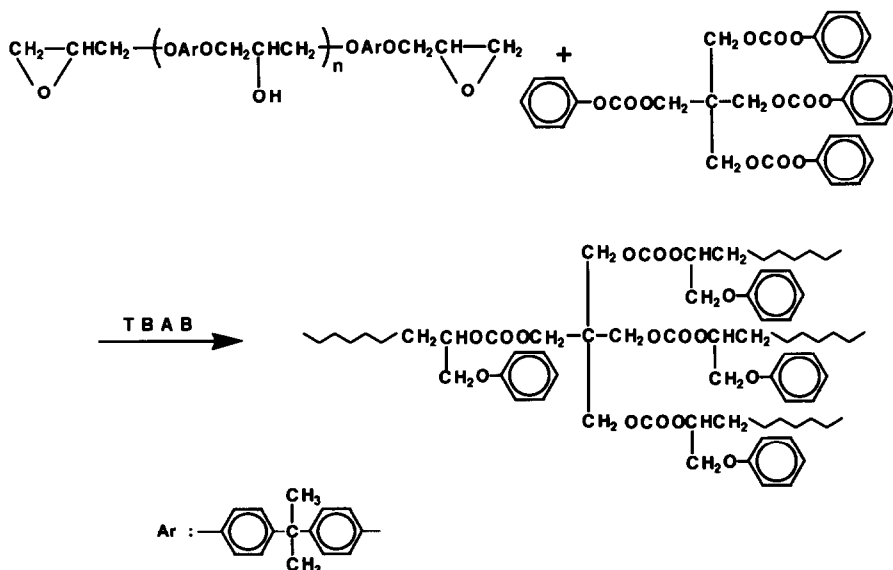
When TAB was used as curing agent, the extent of reaction of epoxide groups became almost constant after 2 h of reaction, irrespective of reaction



Scheme 1.

temperature, and the maximum extent of reaction attained increased with temperature from 27% at 70 °C to almost 100% at 130 °C.

Dynamic DSC scans were carried out with varying concentrations of TBAB catalyst at a heating rate of 3 K min<sup>-1</sup>. As the concentration of catalyst was increased, the maximum peak temperature due to curing



Scheme 2.

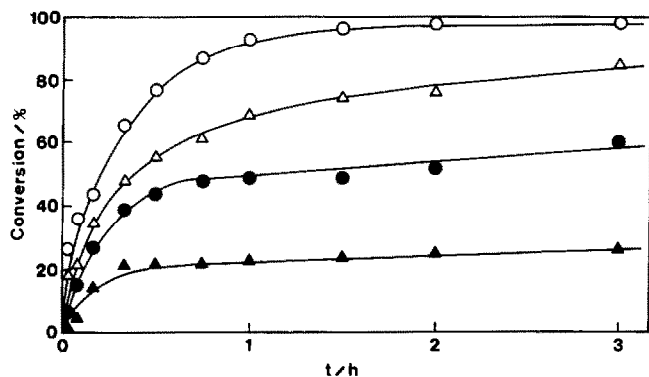


Fig. 1. Conversion vs. reaction time in the curing reaction of BADGE with TAB: BADGE, 0.5 mmol; TAB, 0.33 mmol; TBAB, 2.5 mol%. Reaction temperature: ▲, 70°C; ●, 90°C; △, 110°C, ○, 130°C.

became lower and the curing reaction started and ended at lower temperatures (Fig. 2).

Dynamic curing was then performed at heating rates from 3 to 10 K

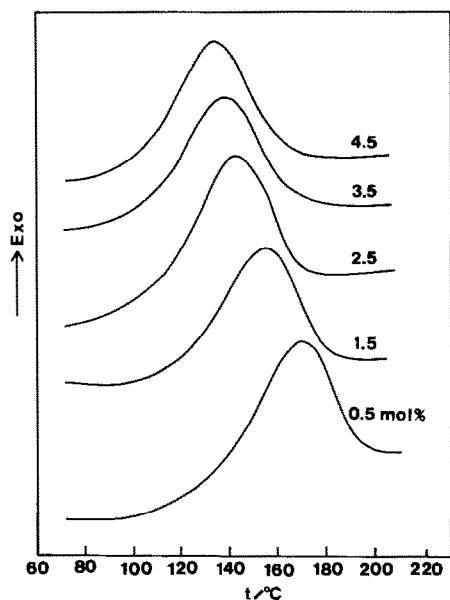


Fig. 2. Effect of catalyst concentration on the curing reaction of BADGE with TAB: BADGE, 0.5 mmol; TAB, 0.33 mmol; heating rate, 3 K min<sup>-1</sup>.

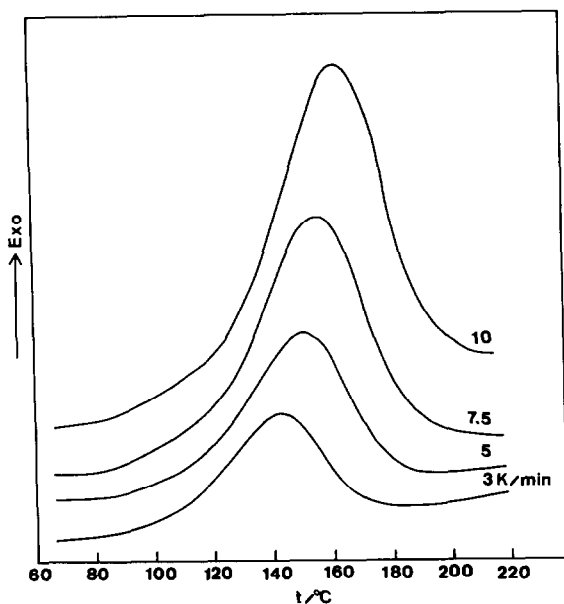


Fig. 3. Effect of heating rate on the curing reaction of BADGE with TAB: BADGE, 0.5 mmol; TAB, 0.33 mmol; TBAB, 2.5 mol.%.

$\text{min}^{-1}$  at a catalyst concentration of 2.5 mol.% (Fig. 3). A linear relationship was obtained when the logarithmic heating rate was plotted against the reciprocal peak temperature of the DSC curves (Fig. 4).

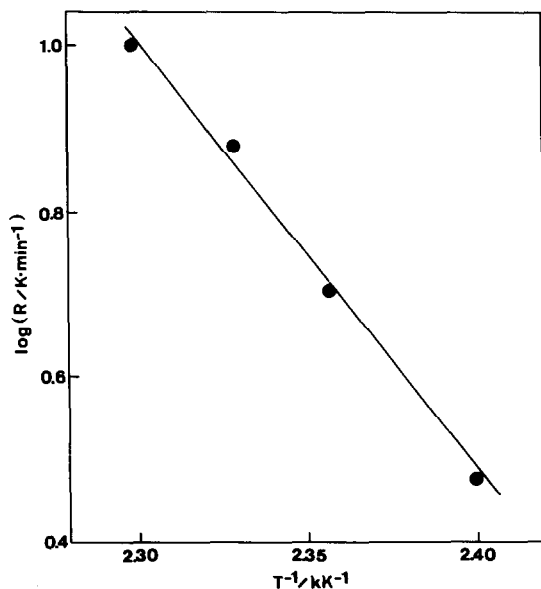


Fig. 4. Logarithmic heating rate  $R$  vs. peak temperature of DSC curves in the curing reaction of BADGE with TAB: BADGE, 0.5 mmol; TAB, 0.33 mmol; TBAB, 2.5 mol.%.

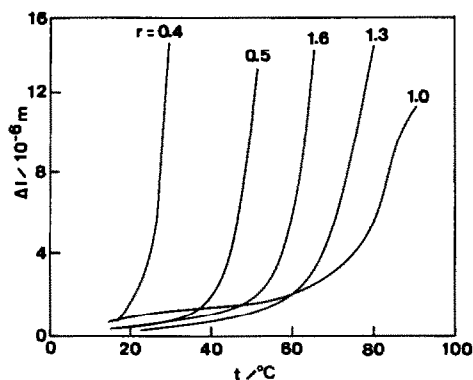


Fig. 5. TMA curves of epoxy resins cured with various ester-to-epoxide ratios  $r$  at  $130^\circ\text{C}$  for 5 h: BADGE, 0.5 mmol; TAB, 0.33 mmol; TBAB, 2.5 mol.%; heating rate,  $3\text{ K min}^{-1}$ .

The activation energy of curing,  $E_a$ , can be obtained according to Ozawa's equation (eqn. (1)) for a non-isothermal process [4]:

$$E_a \approx -2.19R_g \left[ \frac{d \log R}{d(1/T_p)} \right] \quad (1)$$

where  $R_g$  is the gas constant,  $R$  is the heating rate and  $T_p$  is the peak temperature of the DSC curve.

From the slope of the straight line in Fig. 4, the value of  $E_a$  was determined to be  $94.5\text{ kJ mol}^{-1}$  for TAB as curing agent. This is noticeably larger than the values of  $45\text{--}65\text{ kJ mol}^{-1}$  reported for aromatic polyfunctional amines as curing agents [5].

The epoxy systems were then cured at  $130^\circ\text{C}$  for 5 h by varying the stoichiometric ratio  $r$  of ester groups of active ester to epoxy groups of BADGE, and the  $T_g$  values were determined by TMA as the temperature of

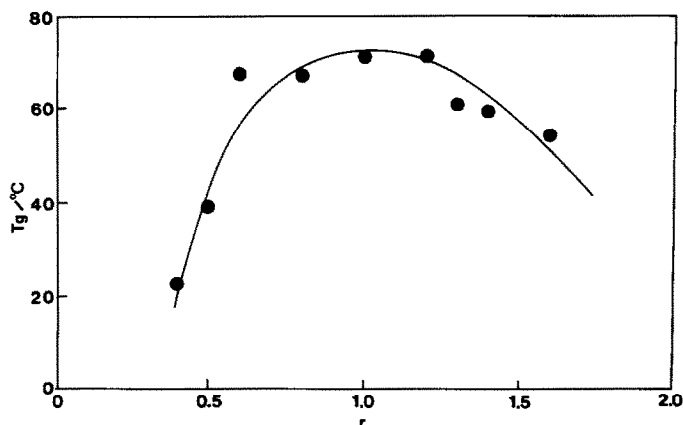


Fig. 6. Effect of  $r$  on the glass transition temperature  $T_g$  of epoxy resins cured with TAB.

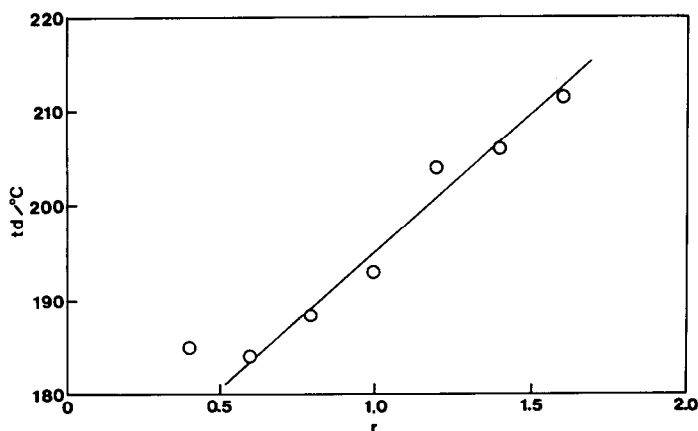


Fig. 7. Effect of  $r$  on the decomposition temperature of epoxy resins cured with TAB.

intersection of the tangent drawn at the greatest slope with the extrapolated baseline (Fig. 5).

Initially the value of  $T_g$  increased and then decreased with an increase in the ratio  $r$ ; the highest  $T_g$  value of  $72^\circ\text{C}$  was obtained for  $r = 1$  (Fig. 6). This result shows the same tendency as reported for diamine-epoxy systems by Galy et al. [6]. If the value of  $r$  is less than unity, then epoxide groups are in excess compared to ester groups and all the ester groups are used up when the reaction is complete. The unreacted epoxide groups lead to pendant chain ends, which are mobile and induce the lowering of  $T_g$ .

With  $r$  greater than unity, unreacted ester groups remain after completion of the reaction because ester groups are present in excess. The distance between cross-links then becomes larger; long chains between cross-links can move more easily than shorter ones, resulting in the lowering of  $T_g$ .

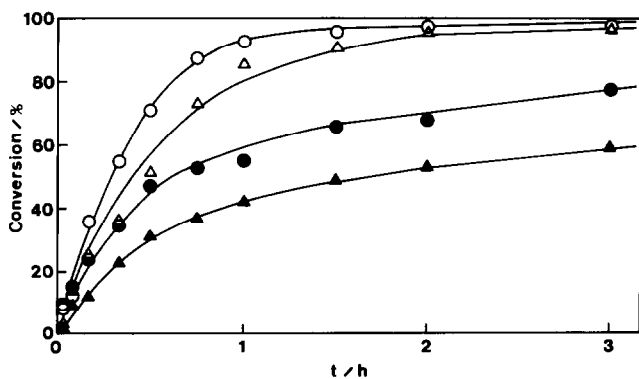


Fig. 8. Conversion vs. reaction time in the curing reaction of BADGE with TPCP: BADGE, 0.5 mmol; TPCP, 0.25 mmol; TBAB, 2.5 mol.%. Reaction temperature: ▲,  $70^\circ\text{C}$ ; ●,  $90^\circ\text{C}$ ; △,  $110^\circ\text{C}$ ; ○,  $130^\circ\text{C}$ .

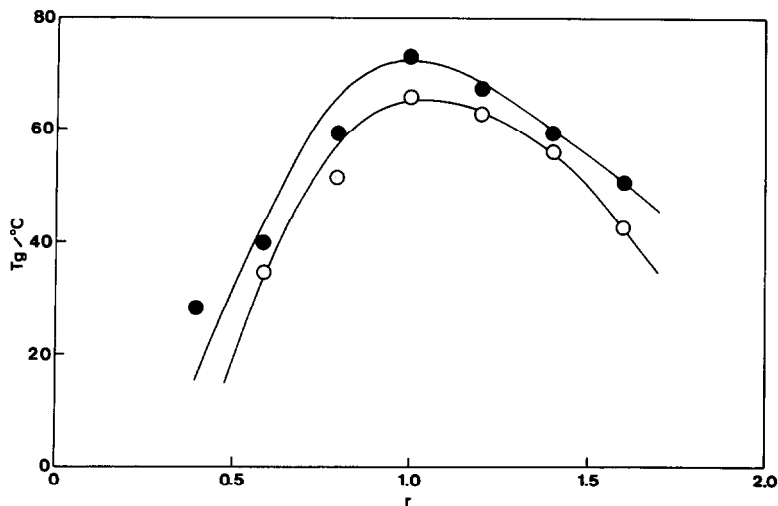


Fig. 9. Effect of  $r$  on the glass transition temperature  $T_g$  of epoxy resins cured with TCP: ○, cured at 110°C for 3 h; ●, cured at 130°C for 5 h.

The thermal stability of the cured resins, determined as the starting temperature of weight loss, increased with increasing  $r$  (Fig. 7).

#### *Curing with tetraphenoxycarbonyl pentaerythritol (TCP)*

The results of isothermal curing of BADGE with TCP are shown in Fig. 8, in which the ratio of ester to epoxide groups was 1:1, the reaction temperature was varied from 70 to 130°C and 2.5 mol.% of TBAB was used as catalyst.

When Fig. 8 was compared with Fig. 1, both the initial rate of reaction

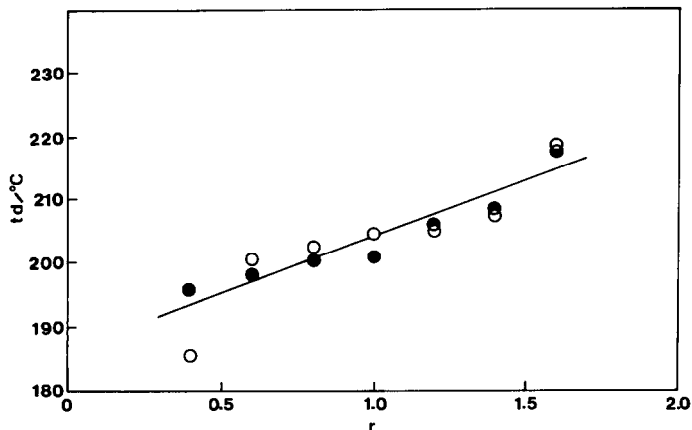


Fig. 10. Effect of  $r$  on the decomposition temperature of epoxy resins cured with TCP: ○, cured at 110°C for 3 h; ●, cured at 130°C for 5 h.



and the maximum extent of reaction attained were seen to be higher for the tetrafunctional TPCP than for trifunctional TAB.

The  $T_g$  of epoxy resins cured with TPCP showed a behavior similar to that of resins cured with TAB. The specimens cured at 130°C for 3 h showed higher  $T_g$  values than those cured at 110°C for 3 h. The highest  $T_g$  value of 72°C was obtained for  $r = 1$  and curing conditions of 130°C and 5 h (Fig. 9). This value is the same as that obtained for the specimen cured with TAB.

The decomposition temperature increased with increasing  $r$  (Fig. 10). This tendency was also observed for TAB curing.

## CONCLUSIONS

1. Both the initial rate of reaction and the maximum extent of reaction are higher for tetrafunctional TPCP than for trifunctional TAB.

2. The highest  $T_g$  value of 72°C is obtained for completely cured specimens at an ester-to-epoxy ratio of  $r = 1$ , irrespective of the curing agent.

3. Thermal stability increases with increasing value of  $r$ .

## REFERENCES

- 1 T. Nishikubo and K. Tanaka, *J. Polym. Sci.*, 26 (1987) 2821.
- 2 H. Weidel and F. Wenzel, *Monatsh. Chem.*, 19 (1889) 249.
- 3 D.R. Moore and G.C. Giuliana, U.S. Patent 3,542,841, 1970.
- 4 T. Ozawa, *J. Therm. Anal.*, 2 (1970) 301.
- 5 F. Miyamoto, K. Osada, S. Oka and H. Nakajima, Proc. 22nd Jpn. Conf. on Calorimetry and Thermal Analysis, The Society of Calorimetry and Thermal Analysis, Tokyo, Japan, 1987, p. 138.
- 6 J. Galy, A. Sabra and J.P. Pascault, *Polym. Eng. Sci.*, 26 (1986) 1514.