

Studies on curing kinetics and thermal stability of epoxy resin *N,N,N',N'*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane using various amine curing agents

Sandeep R. Patel, Vithal S. Patel and Ranjan G. Patel¹

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120 (India)

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Abstract

The curing reactions of tetrafunctional epoxy resin *N,N,N',N'*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane using different amine curing agents has been studied by differential scanning calorimetry. The kinetics of the thermal degradation of the cured epoxy resins were studied by thermogravimetry at a heating rate of 10°C min⁻¹. The overall activation energy for the curing reaction is observed to be in the range 80–207 kJ mol⁻¹.

INTRODUCTION

Epoxy resins containing 4,4'-diamino diphenyl methane (TGDDM) are widely used in the manufacture of high-performance fibrous composites. These resins, with alkyl substituents on the methylene carbon, have been synthesised and studied [1,2]. However, there has been no research on the resin in which a cyclohexane ring replaces the methylene group in the TGDDM structure. In this paper we wish to report the results of our study on the curing reactions of *N,N,N',N'*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane using various amine curing agents and on the thermal stabilities of the cured resins.

EXPERIMENTAL

Materials

The tetrafunctional epoxy resin, *N,N,N',N'*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane, was prepared from a diamine, 1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane [3], following the method re-

¹ Author to whom correspondence should be addressed.

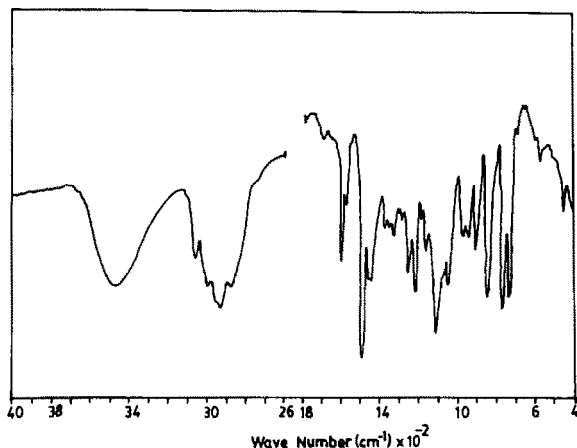
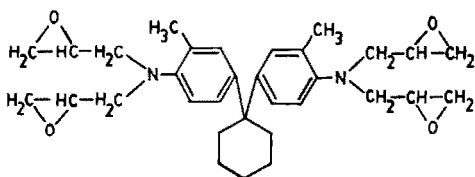


Fig. 1. IR spectra of TGBATC.

ported in the literature [2]. The structure of the resin is shown below



The epoxy equivalent weight as calculated by the hydrochlorination method was found to be 142 g equiv^{-1} . The functionality of this resin, having less than 4 epoxy groups per molecule, was 3.67 per formula weight. The resin was also characterised by IR spectroscopy. The IR spectrum (Fig. 1) shows absorption bands at 3050 and 1190 cm^{-1} which are the characteristics of the aromatic C–H stretching frequency [4]. The absorption bands at 2920 , 2870 , 1450 and 1360 cm^{-1} are attributed to methyl C–H symmetric stretching vibrations. The peak at 1175 cm^{-1} corresponds to C–N stretching frequency. The absorption bands in the regions of 1260 , 920 and 855 cm^{-1} are due to terminal epoxy groups. The bands at 730 and 770 cm^{-1} are attributed to methylene groups.

Curing procedure

The cure temperatures were determined by differential scanning calorimetry (DSC) using a Du Pont 9900 thermal analyser with a DSC module (Du Pont Model 910). The instrument was calibrated with samples of known heats of fusion.

The epoxy resin and the amine were mixed in proportions corresponding to one amine proton per epoxy group. The samples were scanned at a scanning rate of $10^\circ \text{C min}^{-1}$ using an empty cell as reference.

Thermogravimetric analysis (TGA) of the cured epoxy samples

The samples remaining in the test tubes were then cured and kept in a previously heated oven (about 200 °C) for about 2 h for complete curing. The thermograms of the cured products were obtained at a heating rate of 10 °C min⁻¹ for the powdered sample in nitrogen atmosphere. A Du Pont 951 thermogravimetric analyser was used for the study.

Analysis of DSC and TG scans

DSC gives a measure of the differences in the rates of heat absorption by a sample with respect to an inert reference as the temperature is raised at a constant rate. The heat flow data relative to the baseline were processed further to obtain the fractional conversion and the rate of reaction. The method of Borchardt and Daniels [5] allows the calculation of activation energy (E), pre-exponential factor (Z), heat of reaction (ΔH) and order of reaction (n) from a single DSC scan. In addition the activation energy (E) of the TGBATC–TETA system at different heating rates was calculated using Kissinger's method [6]. Borchardt and Daniels' method [5] assumes that the reaction follows n th-order kinetics and that the temperature dependence of the reaction rate follows the Arrhenius expression.

TG curves were analysed to give percentage weight loss as a function of temperature. The activation energy, E , of the degradation process was obtained by Broido's method [7]. Integral procedure decomposition temperature (IPDT) values were obtained using Doyle's method [8].

RESULTS AND DISCUSSION

In order to examine the effect of amine structure on the curing reaction and thermal behaviour of cured tetrafunctional epoxy resin, various diamines such as p,p' -diaminodiphenyl methane (DDM), p,p' -diaminodiphenylamine (DDA), p,p' -diaminodiphenyl sulphone (DDS) and polyamines such as diethylenetriamine (DETA), triethylenetetramine (TETA), ethylenediamine (ED) and butanediamine (BD), were used as curing agents. From the DSC scans, the temperatures at which the curing started, T_i , peaked, T_p , and completed, T_f , and some kinetic parameters such as activation energy, E , pre-exponential factor, $\ln Z$, and order of the curing reaction, were obtained for various epoxy systems and are presented in Table 1.

A comparison of the curing behaviours of different epoxy systems as shown in Table 1 reveals that the values of T_i , T_p and T_f depend on the curing agent. The values are lowest for butanediamine and highest for DDS. This indicates that the rate of curing for the resin–DDS system is the lowest among the systems used. The peak temperature decreases in the order DDS > DDM > DDA > DETA > ED > TETA > BD. The activation en-

TABLE 1

Kinetic parameters of epoxy-amine systems

| Epoxy resin-curing agent system ^a | T_i ^b | T_p ^c | T_f ^d | Borchardt-Daniels relation | | | |
|--|--------------------|--------------------|--------------------|--|----------------------|---------------------------------|------|
| | | | | E (kJ mol ⁻¹) ^e | $\ln Z$ ^e | ΔH (J g ⁻¹) | n |
| TGBATC-DDS | 200 | 243 | 276 | 207.7 | 41.05 | 215 | 2.44 |
| TGBATC-DDM | 125 | 195 | 245 | 111.9 | 27.98 | 289 | 1.35 |
| TGBATC-DDA | 100 | 145 | 200 | 97.4 | 25.38 | 356 | 1.33 |
| TGBATC-DETA | 48 | 117 | 174 | 86.9 | 26.50 | 341 | 1.07 |
| TGBATC-ED | 48 | 115 | 168 | 82.1 | 24.75 | 323 | 1.12 |
| TGBATC-TETA | 46 | 113 | 165 | 81.0 | 24.41 | 352 | 1.41 |
| TGBATC-BD | 45 | 110 | 160 | 80.9 | 24.66 | 412 | 1.33 |

^a Resin, *N,N,N',N'*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane (TGBATC); DDS, *p,p'*-diaminodiphenylsulphone; DDM, *p,p'*-diaminodiphenylmethane; DDA, *p,p'*-diaminodiphenylamine; DETA, diethylenetriamine; ED, ethylenediamine; TETA, triethylenetetramine; BD, butanediamine.

^b T_i , temperature (°C) of the onset of curing.

^c T_p , temperature (°C) of the peak of the exotherm.

^d T_f , temperature (°C) of the completion of curing.

^e Errors in E and $\ln Z$, ± 2 .

ergy values also followed the same order. Selected DSC curves are reproduced in Fig. 2.

An identical trend of the reactivity of the different resin-amine systems can be observed from Fig. 3, in which conversion time (min) is plotted against temperature for 90% conversion. A more reactive system shifts the curve towards a lower temperature than that of a less reactive system. DDS has the lowest reactivity in the series because of the electron-withdrawing

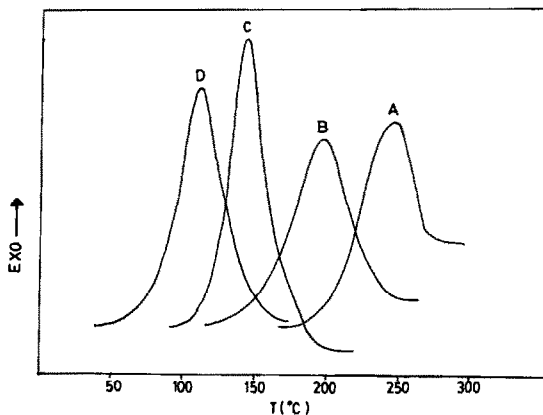


Fig. 2. Dynamic DSC scans at $10^\circ\text{C min}^{-1}$ for the systems: A, TGBATC-DDS; B, TGBATC-DDM; C, TGBATC-DDA; and D, TGBATC-DETA.

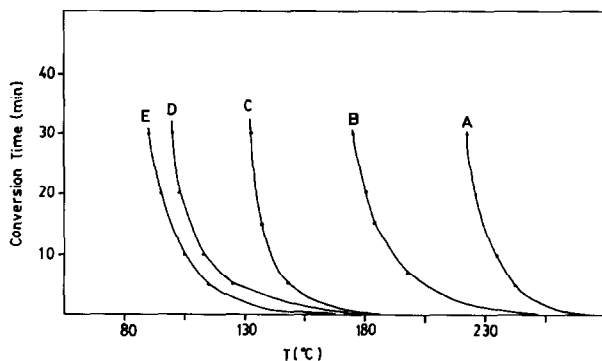


Fig. 3. Plots of conversion time vs. temperature for 90% conversion for the systems; A, TGBATC-DDS; B, TGBATC-DDM; C, TGBATC-DDA; D, TGBATC-TETA; and E, TGBATC-BD.

sulphonyl group. Butanediamine which is purely aliphatic has the highest reactivity. Thus aromatic diamines are less reactive than aliphatic polyamines and, hence, the activation energy of the former is higher than that of the latter.

DSC measurements at different heating rates were also made for the TGBATC-TETA system. Typical DSC scans of rate of heat evolution, dH/dt , as a function of temperature, T , are shown in Fig. 4 for the TGBATC-TETA system containing a stoichiometric amount of TETA. The temperature characteristics, such as the temperatures at which curing started, T_i , peaked, T_p , and completed, T_f , at various heating rates are presented in Table 2. It can be seen that the peak temperature shifts to higher temperatures with increasing scan rate. The values of the total exothermic heat of curing, ΔH , are also presented in Table 2, and can be seen to depend on the scan rate, as observed by Fava [9].

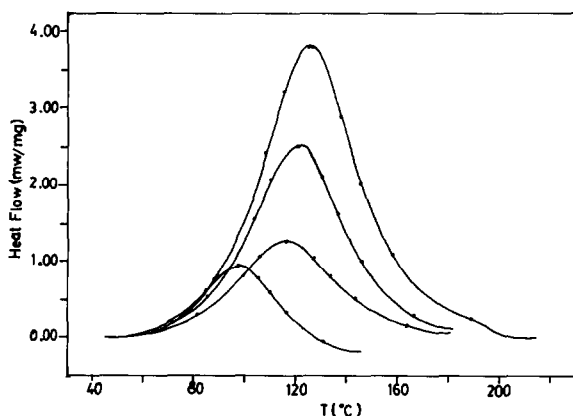


Fig. 4. DSC scans at different heating rates for the system TGBATC-TETA.

TABLE 2

Curing characteristics of TGBATC-TETA resin system at various scan rates

| Heating rate ($^{\circ}\text{C min}^{-1}$) | Temperature characteristics ($^{\circ}\text{C}$) | | | E (kJ mol^{-1}) | ΔH (J g^{-1}) |
|---|--|--------|-------|------------------------------|-------------------------------------|
| | T_i | T_p | T_f | | |
| 5 | 40.1 | 98.19 | 145.0 | 36.8 | 302.9 |
| 10 | 45.6 | 113.00 | 180.4 | | 354.6 |
| 15 | 49.1 | 121.57 | 182.3 | | 451.9 |
| 20 | 50.8 | 125.50 | 214.7 | | 578.7 |

The plots of $\log(\text{heating rate})$ against reciprocal temperature for TGBATC-TETA at a scan rate of $5^{\circ}\text{C min}^{-1}$ are shown in Fig. 5 which displays an unexpectedly high degree of linearity. Hence it is reasonable to assume that any change in the curing mechanism with curing temperature does not affect the overall reaction rate.

The plots of percentage conversion against time and conversion time against temperature are given in Figs. 6 and 7 respectively. It is observed from Fig. 6, that an increase in temperature results in a decrease in conversion time. From Fig. 7, the time required to achieve a particular conversion degree at a definite temperature can be identified.

Selected thermograms obtained under dynamic conditions at a heating rate of $10^{\circ}\text{C min}^{-1}$ are reproduced in Fig. 8. In order to determine the thermal stability trend, TG parameters such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT (integral procedure decomposition temperature) and the activation energy, E , of the degradation process were calculated.

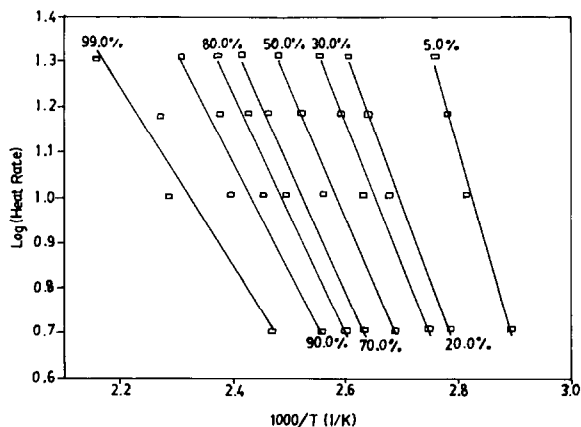


Fig. 5. Plots of $\log(\text{heating rate})$ vs. reciprocal temperature for the system TGBATC-TETA at a scan rate of $5^{\circ}\text{C min}^{-1}$.

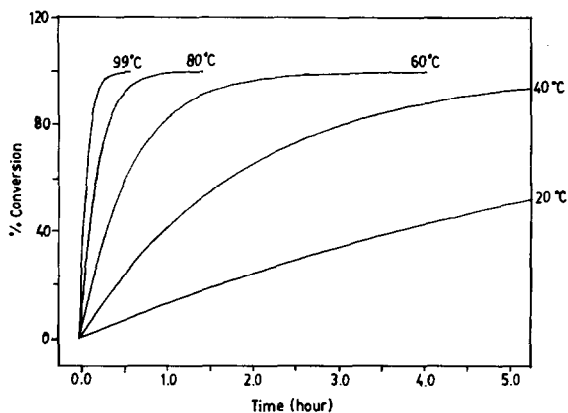


Fig. 6. Plots of %conversion vs. time at different temperatures for the system TGBATC-TETA at a scan rate of $5^{\circ}\text{C min}^{-1}$.

T_0 and T_{10} are two of the main criteria used to indicate the heat stability of polymers. The higher the values of T_0 and T_{10} , the higher the thermal stability of the system [10]. However, T_0 , T_{10} and T_{\max} are single features of the TGA curves. To obtain a quantitative picture of the relative stability, the IPDT values can be regarded as being of significant importance, as they represent the overall nature of the TGA curves.

The thermal stability of amine-cured epoxy systems is most affected by the structure of the amine used as curing agent. The trend in the thermal stability for the amine-cured epoxy resins as shown in Table 3 is TGBATC-DDS > TGBATC-DDM > TGBATC-DDA > TGBATC-BD > TGBATC-ED > TGBATC-TETA > TGBATC-DETA. The curing agents DDM and DDS gave relatively more stable cured resins because of the thermally stable linkages present within the aromatic nuclei [11,12]. The greater stability of

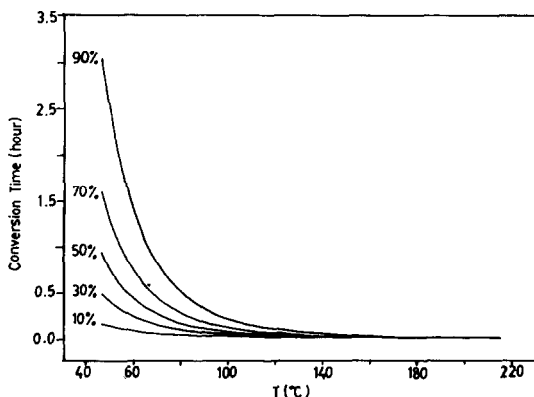


Fig. 7. Plots of conversion time vs. temperature for different %conversion for the system TGBATC-TETA at a scan rate of $5^{\circ}\text{C min}^{-1}$.

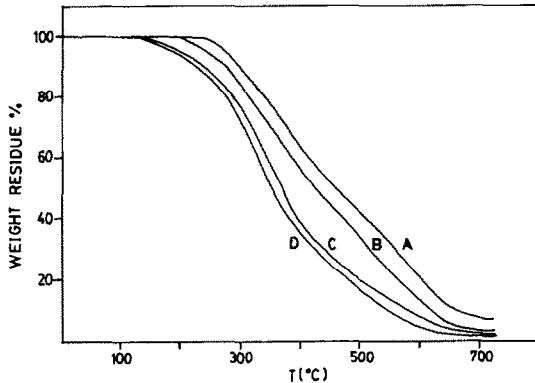


Fig. 8. TG curves for cured epoxy systems in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$; A, TGBATC-DDS; B, TGBATC-DDM; C, TGBATC-TETA; and D, TGBATC-DETA.

TABLE 3

Temperature characteristics and kinetic parameters of cured epoxy resins

| Epoxy resin-curing agent system ^a | T_0 ($^{\circ}\text{C}$) | T_{10} ($^{\circ}\text{C}$) | T_{20} ($^{\circ}\text{C}$) | T_{40} ($^{\circ}\text{C}$) | T_{60} ($^{\circ}\text{C}$) | T_{max} ($^{\circ}\text{C}$) | IPDT ^b ($^{\circ}\text{C}$) | E^c (kJ mol^{-1}) |
|--|---------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|--|---|-----------------------------------|
| TGBATC-DDS | 250 | 300 | 337 | 412 | 512 | 462 | 532 | 70.7 |
| TGBATC-DDM | 200 | 275 | 312 | 387 | 475 | 450 | 477 | 60.2 |
| TGBATC-DDA | 175 | 262 | 300 | 375 | 450 | 413 | 460 | 51.8 |
| TGBATC-BD | 162 | 250 | 291 | 350 | 410 | 378 | 451 | 46.0 |
| TGBATC-ED | 150 | 237 | 288 | 338 | 387 | 352 | 440 | 43.1 |
| TGBATC-TETA | 137 | 232 | 285 | 335 | 385 | 338 | 434 | 41.8 |
| TGBATC-DETA | 125 | 225 | 275 | 325 | 376 | 322 | 425 | 36.9 |

^a See Table 1 for the meanings of the abbreviations for the epoxy resin-curing agent systems.

^b IPDT, integral procedure decomposition temperature.

^c Error, ± 2 .

the DDS-cured resin may be ascribed to the greater heat resistance of the sulphur links compared with those of carbon [12]. The lowest stability observed in the case of the TGBATC-DETA system is due to the purely aliphatic structure of DETA in the cured product. The trend in the thermal stabilities of the cured resins can also be deduced from the values of the activation energy, E .

CONCLUSION

The curing reactions of the epoxy-amine systems have an activation energy in the range $80.9\text{--}207.7\text{ kJ mol}^{-1}$. The thermogravimetric study of various cured epoxy systems reveals that the thermal stability depends on

the structure of the curing agent used. The activation energy of the thermal degradation is in the range 36.9–70.7 kJ mol⁻¹.

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