

Multifunctional Epoxy Resins: Synthesis and Characterization

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Received 14 September 1999; accepted 17 December 1999

ABSTRACT: The tetrafunctional epoxy resins were prepared starting from diaminodiphenylmethane, diaminodiphenylether, and diaminobibenzyl. The obtained resins were characterized by IR and $^1\text{H-NMR}$ spectroscopy, rheological and thermal techniques. The polymerization reaction was investigated by viscosimetry. The flow activation energy and the polymerization activation energy were evaluated from the rheological data and from the critical parameters (critical time and critical viscosity at gel point). The viscosity measurements and gel time determination showed slight differences between the synthesized resins. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2430–2436, 2000

Key words: tetrafunctional epoxy resins; crosslinking reaction; rheological and thermal properties

INTRODUCTION

Epoxy resins are the most versatile compounds used as structural adhesives and matrix resins in numerous applications including civil engineering, machinery, aero- and hydro-space engineering, agriculture, medicine, and so on. Because the properties of the composites are dominated by the structure of the matrix resins, intensive research efforts have been devoted to develop new epoxy resins or chemical and physical modification of the classical resins in the last years.^{1–7}

The multifunctional epoxy resins are used in military and civilian applications because their higher crosslinked structure showed improve thermal, mechanical, and adhesion performance.^{8–11} There are some reports regarding the preparation of the multifunctional epoxy derivatives.^{12–17}

The aim of this article is to report the synthesis of some tetrafunctional epoxy resins and their characterization by IR and $^1\text{H-NMR}$ spectroscopy. The rheological and thermal behavior of these polymers are also emphasized.

EXPERIMENTAL

Materials

4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylether (DDE), triethylenetetramine (TETA), potassium hydroxyde (KOH), and sodium hydroxide (NaOH) were analytical grades and were used as received.

4,4'-Diaminobibenzyl (DBBz) was a commercial product purified by recrystallized from ethanol twice before use.

Epichlorohydrin and organic solvents were chemically pure reagents and were used without further purification.

Measurements

The epoxy equivalent of tetrafunctional epoxy resins was expressed in $\text{g} \cdot \text{eq}^{-1}$ and determined

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Journal of Applied Polymer Science, Vol. 77, 2430–2436 (2000)
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by Sandner method.¹² ¹H-NMR spectra were obtained with the aid of JEOL-JNMC 60HL equipment (Japan) at 50°C. Samples were run using CDCl₃ as solvent and tetramethylsilane as internal standard. IR spectra were recorded with a Specord M80 (Carl Zeiss) spectrophotometer (KBr pellets). Thermal studies were made with a MOM Budapest derivatograph of Paulik, Paulik-Erdey type at a heating rate of 12°C/min.

Rheological behaviors were performed using Rheotest 2.1 (Germany) type viscometer equipped with a cone and plate device, with a cone diameter of 36 mm and angle of 0.3° at 1 s⁻¹ shear rate and temperature intervals ranging between 20 and 80°C.

The curing agent was TETA in a $r = 0.75$ ratio, where “ r ” is defined as $r = \text{amine hydrogen/epoxy group}$.

The apparent shear viscosity was evaluated for all the synthesized resins using Eq. (1)¹⁸:

$$\eta_{ap} = \tau \cdot \gamma^{-1} \quad (1)$$

where τ is the shear stress and γ is the shear rate (s⁻¹). The zero shear rate viscosity, k (consistency index), and the flow index (n), were obtained from the logarithmic graph $\log \tau$ versus $\log \gamma$ using the Ostwald de Waele model¹⁹:

$$\tau = k \cdot \gamma^n \quad (2)$$

The flow activation energy ($E\gamma$) was evaluated using Arrhenius equation:

$$\eta_{ap} = A \exp(E\gamma/RT) \quad (3)$$

where A is a constant characteristic of the sample, R is the gas constant, and T is temperature in °K.

The crosslinking reaction was characterized by change of the viscosity as function of time at constant temperature and shear rate. Using the initial viscosity of the sample and variation of the viscosity with the time, the critical value for the viscosity (η_c) and time (t_c) corresponding to the gel point were calculated.²⁰

The apparent activation energy for the curing process can be calculated from the slope of the lines using the logarithmic graph $\ln t_c$ versus $1/T$.

Synthesis of the Tetraglycidyl of Diaminodiphenylmethane (TGDDM)

A 4-necked round-bottomed flask equipped with mechanical stirrer, thermometer, dropping fun-

nel, and water condenser was charged with 24.75 g (0.125 mol) DDM, 186 g (2 mol) epichlorohydrin, 45 mL ethanol, and 9 mL water. The mixture was stirred and slowly heated on the water bath to 75°C and held for 6 h. The reaction mass was cooled to 54–56°C and 16 g NaOH (0.4 mol) as 30% w/w aqueous solution was slowly added to the mixture over a 5-h reaction time. The mixture was then distilled to remove the ethanol, water, and epichlorohydrin. In order to separate the salt from crude product, 100 mL of toluene was added. The suspension was filtered and the organic phase was distilled under vacuum at 130°C, to remove the residual epichlorohydrin, water, and toluene. Finally, a pale brown resin (46.8 g, yield 88%) resulted, having the epoxy equivalent weight 114 g · eq⁻¹.

IR (KBr) cm⁻¹: 1620 (phenyl), 1250–1270 (C—N aromatic), 1150–1200 (C—N aliphatic), 915 (oxirane ring), 840 (p-substituted benzene).

¹H-NMR (CDCl₃) ppm: 2.65 (multiplet, CH₂ oxirane ring protons), 3.15 (singlet, CH oxirane ring proton), 3.6 (multiplet, NH proton), 6.70–7.1 (aromatic protons).

Synthesis of the Tetraglycidyl of Diaminodiphenylether (TGDDE)

DDE, 20.2 g (0.1 mol), was dissolved in 30 mL of dimethylformamide, 186 g (2 mol) of epichlorohydrin, and 7.2 g of water was charged in a four-necked flask fitted with mechanical stirrer, thermometer, water condenser, and dropping funnel. The mixture was gradually heated on the water bath to 60°C and maintained for 12 h. Then, the temperature was decreased to 42°C and 23.2 g of KOH of aqueous solution of 30% w/w was added in over 3 h, while maintaining the reaction mass at 40–42°C. The mixture was then filtered and the organic phase was washed several times with distilled water and evaporated under vacuum at 135°C. Finally, 50 mL of toluene was added and the azeotrope of epichlorohydrin with toluene and toluene was distilled under vacuum. A dark viscous resin was obtained, 34.4 g (yield 79%) with the epoxy equivalent weight 111 g · eq⁻¹.

IR (KBr) cm⁻¹: 1615 (phenyl), 1235 (C—N aromatic), 910 (oxirane ring), 830 and 755 (p-substituted benzene).

¹H-NMR (CDCl₃) ppm: 2.81 (multiplet, CH₂ oxirane ring protons), 3.08 (singlet, CH oxirane ring proton), 3.6 (multiplet, NH proton), 4.05 (multiplet N—CH protons), 6.66–7.31 (aromatic protons).

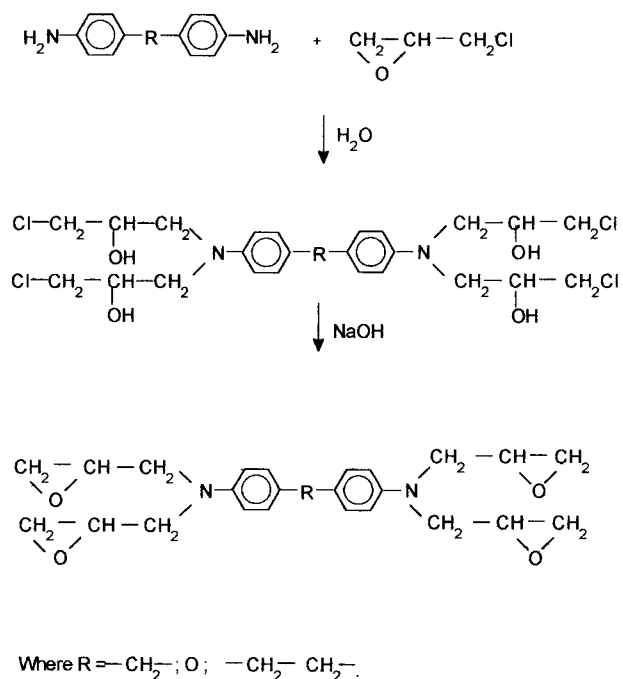
Synthesis of the Tetraglycidyl of Diaminobibenzyl (TGDBBz)

A similar setup was charged with 21.32 g (0.1 mol) diaminobibenzyl (DBBz), 40 mL of ethanol, 186 g (2 mol) of epichlorohydrin, and 7.2 g of water. The mixture was stirred and heated on the water bath to 60°C and held 7 h. Then, the temperature was decreased at 50°C when the 16 g of NaOH of aqueous solution of 30% w/w was added dropwise, while the temperature was maintained at 50–52°C for 3 h. The salt was filtered and the organic phase was washed with distilled water to a neutral point. Finally, the reaction mass was diluted with toluene and evaporated under reduced pressure. Result 35.2 g (yield 81%), a semi-solid deep brown resin with the epoxy equivalent weight 116 g · eq⁻¹.

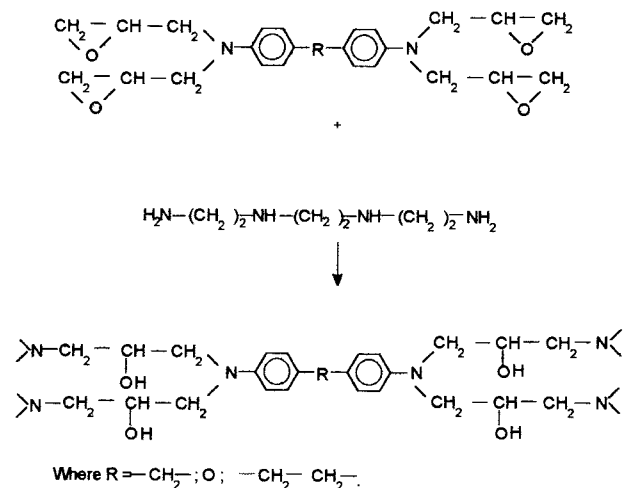
IR (KBr) cm⁻¹: 1615(aromatic), 1240–1260 (C–N aromatic), 1160–1195 (C–N aliphatic), 910 (oxirane ring), 835 and 710 (p-substituted benzene).

¹H-NMR (CDCl₃) ppm: 2.7–2.85 (multiplet, CH₂ oxirane ring protons), 3.10 (singlet, CH oxirane ring proton), 3.55 (multiplet, NH proton), 4.05 (multiplet N–CH₂ protons), 6.75–7.25 (aromatic protons).

All of the reactions involving these products are presented in Scheme 1.



Scheme 1



Scheme 2

Curing of Tetraglycidyl Resins

Curing reactions were performed with TETA by mixing the components in the ratio $r = 0.75$ where $r = \text{amine hydrogen/epoxy group}$ at 1 s⁻¹ shear rate and temperature intervals ranging between 20 and 50°C. The chemical reactions are presented in Scheme 2. The obvious absence of terminal epoxy group in the IR spectra confirmed the crosslinking of resins.

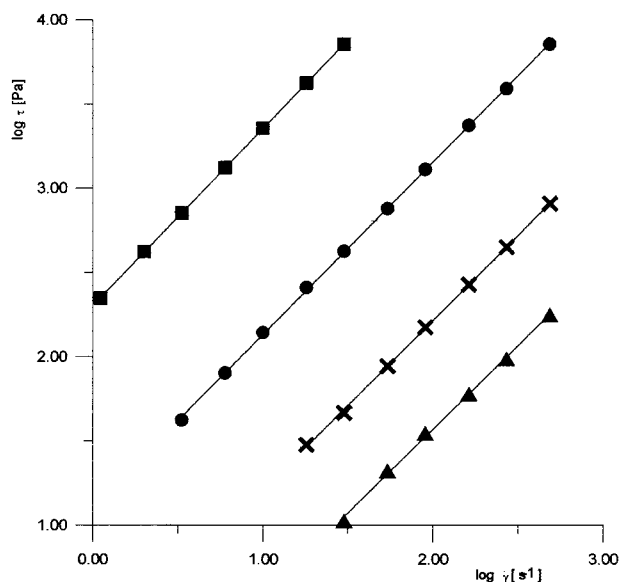


Figure 1 Variation of the shear stress versus shear rate for the TGDDM resins. Temperatures: (■) 20°C; (●) 40°C; (X) 60°C; (▲) 80°C.

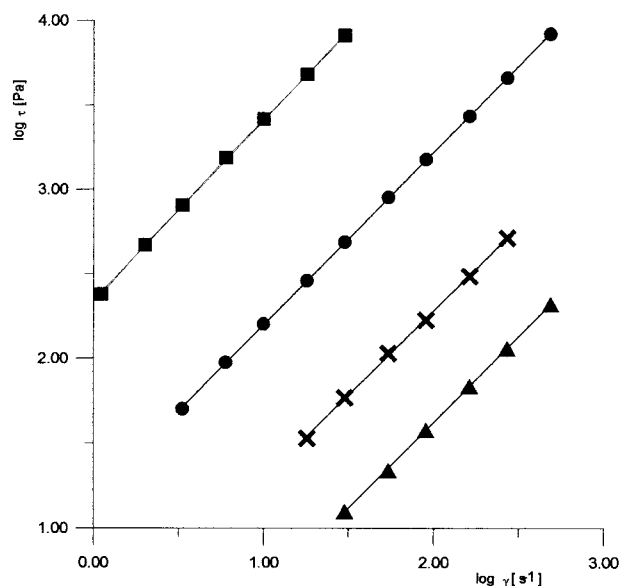


Figure 2 Variation of the shear stress versus shear rate for the TGDFE resins. Temperatures: (■) 20°C; (●) 40°C; (X) 60°C; (▲) 80°C.

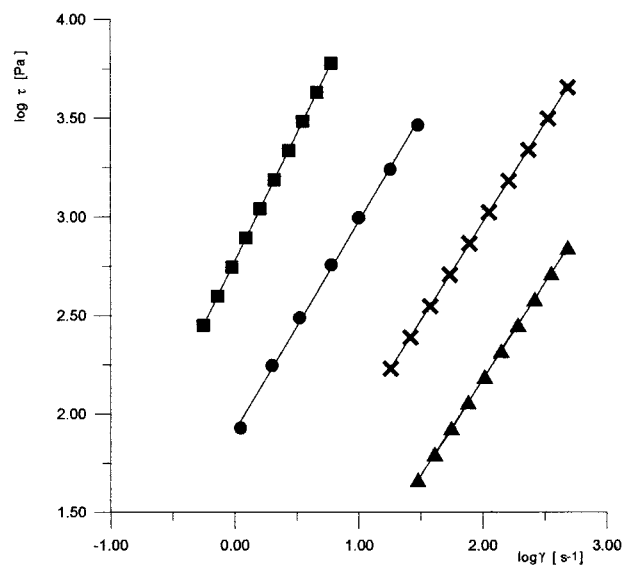


Figure 3 Variation of the shear stress versus shear rate for the TGBBz resins. Temperatures: (■) 20°C; (●) 40°C; (X) 60°C; (▲) 80°C.

RESULTS AND DISCUSSION

Tetraglycidyl resins were synthesized from aromatic diamines and epichlorohydrin using NaOH or KOH as catalyst to obtain the epoxy ring. The reaction was conducted in two steps in a large excess of epichlorohydrin with the aim of obtaining an epoxy resin with a low molecular weight. The obtained resins are semisolid and are soluble in both the medium and the highly polar solvents.

The structures of the resins were confirmed by IR and $^1\text{H-NMR}$ spectra. The peaks of the oxirane ring in IR spectra were observed in $910\text{--}925\text{ cm}^{-1}$ interval. The peaks centered at 1660 cm^{-1} and 840 cm^{-1} are specific for the aromatic ring *p*-substituted. After curing, the peak specific of

oxirane ring disappeared. In the $^1\text{H-NMR}$ spectra, the signal of the protons assigned to the glycidyl group are located at 2.5–2.8 ppm chemical shifts for the protons located at CH_2 situated in oxirane ring. The peaks situated at 3.1–3.2 ppm are attributed to the protons placed in the CH group and the protons situated near N are located at 3.55–4.1 ppm. The aromatic protons resonate as a complex pattern in the range 6.65–7.4 ppm.

Rheological Behavior

The rheological experimental data were used to plot $\log \tau$ versus $\log \dot{\gamma}$ for the synthesized resins. In Figures 1–3, the extrapolation of the straight lines to $\gamma = 0$ and the slope was used to obtain the

Table I Variation of the Consistency Index, Flow Index, and Flow Activation Energy in the Temperature Range 20–80°C

Sample	Temperature (°C)								Flow Activation Energy ($\gamma = 0$) (Kj/mol)	Flow Activation Energy ($\tau = 250\text{ Pa}$) (Kj/mol)
	20		40		60		80			
	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>		
TGDDM	202	1.05	12.7	1.025	1.57	1.009	0.405	0.96	89.45	90.1
TGDDE	222	1.065	15.2	1.020	1.97	1.01	0.41	1.00	90.20	90.88
TGBBz	588	1.28	87.4	1.031	9.75	1.00	1.70	0.97	84.97	84.64

k, Pas.

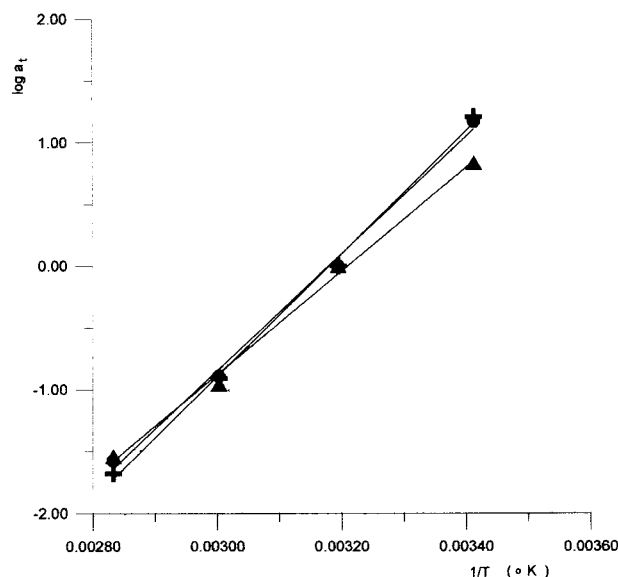


Figure 4 Variation of the shift factor with reciprocal of temperature. (●) TGDDM; (○) TGDDE; (△) TGDBz.

consistency index (k) and the flow index (n). The values of both the consistency index and the flow index are listed in Table I. As can be seen, the flow index has values higher than 1 at 20°C, which is in concordance with a non-Newtonian behavior of dilatant type. At high temperature (80°C) the flow indices tend toward 1 and the rheological behavior becomes Newtonian. This fact might be because of formation of intermolecular complexes at low temperature leading to an apparent increase in molecular weight. With the increase in temperature, the mobility of the molecules also increases, the networks are broken, and the rheological behavior becomes Newtonian. The increase of the viscosity of TGDBz compared with TGDDM and TGDDE can be explain

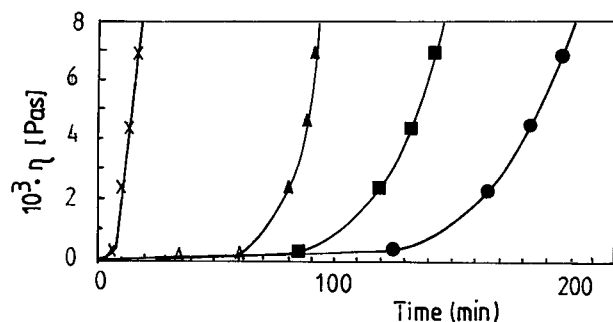


Figure 5 Variation of the viscosity versus time for TGDDM resin. Temperatures: (●) 20°C; (■) 30°C; (▲) 40°C; (X) 50°C.

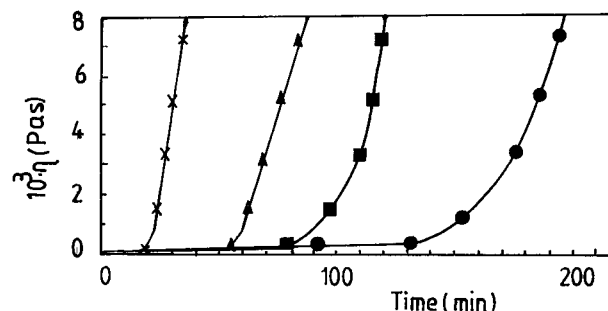


Figure 6 Variation of the viscosity versus time for TGDFE resin. Temperatures: (●) 20°C; (■) 30°C; (▲) 40°C; (X) 50°C.

by the fact that the bibenzyl structures are more rigid compared with the structures of DDM and DDE.²⁰

The activation energy for the flow at zero shear rate and at $\tau = 250$ Pa, was calculated using the Arrhenius Eq. (3) from the slope of the plots $\log k$ versus $1/T$. The values of the activation energy for the flow calculated at temperature in the range 20–80°C are listed in Table I. These were almost constant values for all the synthesized resins. Similar values were obtained when the activation energy for the flow at zero shear rate is calculated using the shift factor (temperature reference = 293 K) (Fig. 4).

The resin/hardener system was polymerized at different temperatures. Figures 5–7 represent the development of the curing processes versus temperature and time. The curing process is characterized in a first stage by a linear increase in viscosity. In the second stage following the crosslinking a sharp increase in viscosity is observed. The critical values evaluated for the viscosity and the time at the gel point (the gel point may be considered a relative measure of the rate

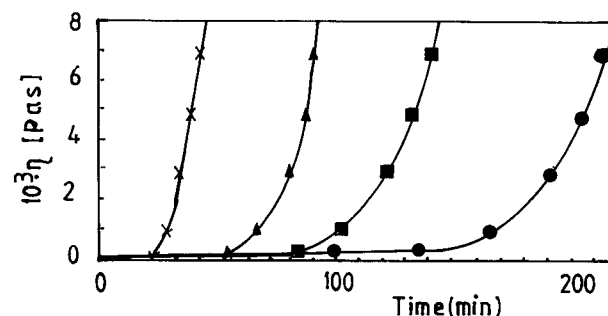


Figure 7 Variation of the viscosity versus time for TGDBz resin. Temperatures: (●) 20°C; (■) 30°C; (▲) 40°C; (X) 50°C.

Table II Variation of the Critical Time and Critical Viscosity in the Temperature Range 20–50°C

Sample	Temperature (°C)								Curing Activation Energy (Kj/mol)
	20		30		40		50		
	t_c	η_c	t_c	η_c	t_c	η_c	t_c	η_c	
TGDDM	130	450	85	389	68	181	10	88	61.40
TGDDE	143	410	80	283	53	110	18	62	47.22
TGDBz	135	520	105	190	56	90	25	67	44.30

t_c , minutes; η_c , Pas.

of bond formation into polymer chains) was obtained according to the Liska method,²¹ and are presented in Table II. As can be seen in Table II, the critical time and the critical viscosity do not differ much from one system to another. This behavior can be explained by the fact that the structures of the resins are similar.

The apparent activation energies of the curing process obtained from the graph $\ln t_c$ versus $1/T$ are presented in Table II and have values comparable with the data in the literature.²²

Thermal Characterization of the Cured Resins

The thermal behaviors of the cured polymers were studied by thermogravimetry analysis. The

samples were cured at room temperature and after curing were maintained at 120°C for 2 h. Thermogravimetry curves and the most important parameter are shown in Figure 8 and in Table III. It can be seen that the crosslinking resins exhibit a reasonable thermal stability up to 320°C. The TGDDM had a higher thermal stability compared with TGDDE and TGDBZ. The apparent thermal stability of these cured resins was evaluated using the decomposition activation energy calculated with the Coats and Redfern method for an order of reaction $n = 1$.²³ The decomposition activation energies are listed in Table III. As can be seen, the values do not differ much because the structures of the resins are comparable.

CONCLUSION

The tetraglycidyl resins were synthesized by reaction between aromatic diamines (dissolved in polar solvents to achieve homogenous reaction masses) and epichlorohydrin in a large excess. The resulted polymers are semisolid at room temperature (20°C) and are soluble in common polar solvents.

The rheological behavior is of thixotropic type at room temperature and tends to the Newtonian or pseudoplastic type when the temperatures increase. This fact can be due to the interpenetrating of the glycidyl chain at 20°C with its destruction when the temperature is increased.

The flow activation energies in a 20–80°C temperature interval have values in a range of 84.97–90.2 Kj/mol and are comparable with the data in the literature.²²

The apparent energies for the curing have values ranging between 44.3 and 61.4 Kj/mol for the temperature interval 20–50°C.^{24,25}

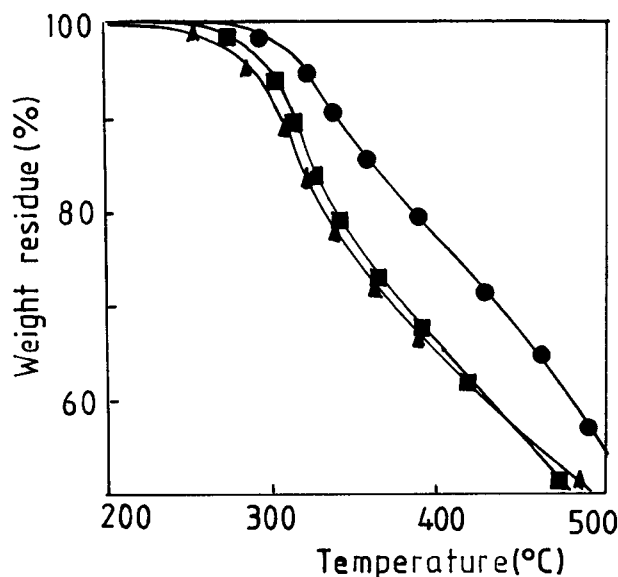


Figure 8 TG curves for decomposition in air of (X) TGDDM; (●) TGDDE; (▲) TGDBBz.

Table III Thermal Parameters of Crosslinked Resins

Sample	Weight Loss at Temperature (°C)		Weight Loss at 500°C (%)	Decomposition Activation Energy (Kj/mol)
	10 (%)	50 (%)		
TGDDM	350	530	45	48.90
TGDDE	320	480	52	50.80
TGBBz	320	480	55	59.01

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