

Cure and Thermal Properties of Brominated Epoxy Systems

HEMI N. NAÉ,* *Department of Materials Research, The Weizmann Institute of Science, Rehovot, Israel 76100*

Synopsis

The addition of a brominated epoxy resin as a chain extender to di-, tri-, and tetrafunctional epoxy systems cured with diaminodiphenylsulfone has been investigated. The effect of increased BER content on the glass transition temperature of the cross-linked systems is discussed. The T_g of these systems is in the order T_g (tri) > T_g (tetra) > T_g (di). The contributions of the chemical structure and the cross-link density to the glass transition temperature are calculated. The kinetics of the reaction was followed dynamically by DSC. The overall order of the reaction and activation energies decrease with increased BER content. The thermal stability of these systems is also discussed.

INTRODUCTION

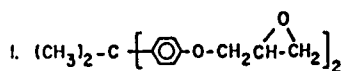
The development of improved thermosetting systems is important in a variety of applications, including coatings, adhesives, materials for the electronics industry and high-performance fiber-reinforced composites. The toughness and thermal stability of such systems depend on the chemical structure of the thermosetting resin and the curing agent and on the conditions of polymerization: time and temperature.^{1,2} To improve their toughness, chain extenders such as telechelic reactive butadiene-acrylonitrile copolymers,³ bisphenol A⁴ brominated epoxy resins,⁵ and butylacrylate-acrylic acid copolymers⁶ have been introduced. The improved toughness of rubber-modified systems has been attributed to elastomer domains dispersed in the cross-linked matrix.⁷ Incorporation of brominated epoxy resins in thermosetting systems imparts flame retardancy and may improve their toughness. It is the objective of this research to characterize the cure behavior and thermal properties of systems containing brominated epoxy resins and the effect of the bromine content on these properties.

EXPERIMENTAL

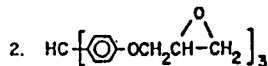
Materials

Diglycidyl ether of bisphenol A, DR (DER 332), and triglycidyl ether of tris (hydroxyphenyl) methane, XD (XD 7342), both from the Dow Chemical Company, and tetraglycidyl diaminodiphenylmethane, MY (MY720), Ciba-Geigy, were the epoxy resins. A brominated epoxy resin, BER (F2001P), Makhteshim Chemical Works, was the chain extender. Diaminodiphenylsul-

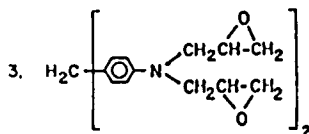
*Incumbent of the Steinfeld Career Development Chair.



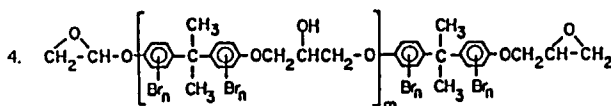
DIGLYCIDYL ETHER OF BISPHENOL A, DR



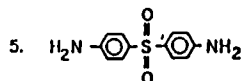
TRIGLYCIDYL ETHER OF TRIS (HYDROXY PHENYL) METHANE, XD



TETRAGLYCIDYL 4,4' DIAMINO DIPHENYL METHANE, MY



BROMINATED EPOXY RESIN, BER



DIAMINO DIPHENYL SULFONE, DDS

Fig. 1. Formulas of raw materials.

fone, DDS, Aldrich, was the curing agent. No catalyst has been added. DDS was added to form stoichiometric compositions (one amine hydrogen per epoxy group). Each formulation was dissolved in 1:10 w/v in methyl ethyl ketone. Samples were cured isothermally in aluminum pans for 24 h and cooled to room temperature. The formulas of the raw materials are shown in Figure 1.

Thermal Properties

Thermal properties were measured on a Mettler 3000 system. DSC scans were under nitrogen flow at 10°C/min. Thermogravimetric analysis was under nitrogen flow at 20°C/min.

RESULTS AND DISCUSSION

A difunctional brominated epoxy resin (BER) was chosen as a chain extender for this research since it participates in the polymerization process through its epoxy groups rather than through carboxyl or hydroxyl groups. The incorporation of BER in epoxy systems and their cure behavior were studied by following the thermal properties of samples that were cured isothermally. All the cured systems were transparent and did not exhibit phase separation. This is an indication of the compatibility of BER with these

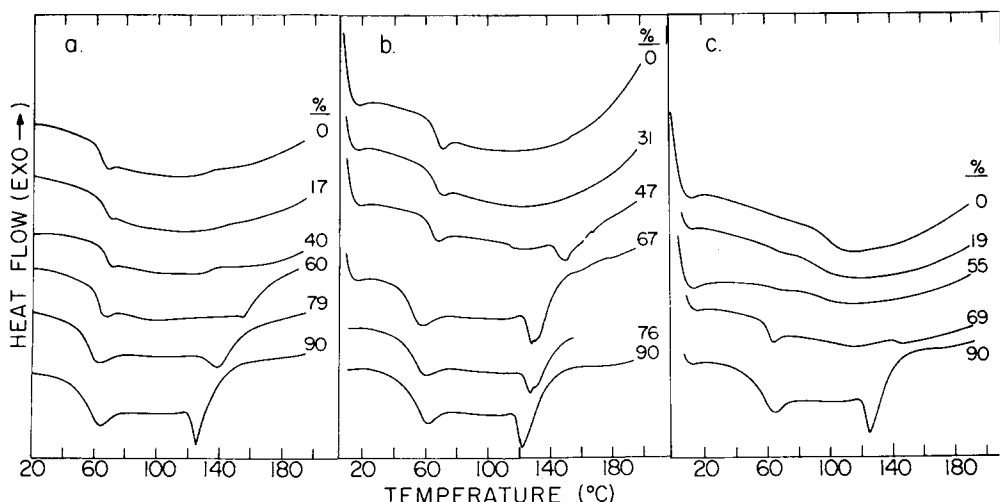


Fig. 2. Representative DSC scans of three epoxy systems cured at 80°C: (a) DR, (b) MY, (c) XD, with various BER contents.

systems. The modified systems were designed to meet flame retardancy requirements (UL 94 V-0).

Effect of Cure Temperature and BER Content on the Glass Transition Temperature

Representative DSC scans of systems containing a difunctional epoxy resin (DR), a trifunctional resin (XD), and a tetrafunctional resin (MY) cured with various amounts of BER at 80°C are shown in Figure 2. These systems reach vitrification well before they are fully polymerized. The result is a low glass transition temperature T_g (about 60°C). A second transition is observed upon scanning to higher temperatures (above 120°C). The first transition occurs well below the ultimate T_g , $T_{g\infty}$, and depends on the temperature of cure and on the structure of the epoxy resin. Although there is almost no effect of BER content on the T_g in systems containing DR and MY, there is a decrease in the T_g in systems containing XD with a high BER content. At low cure temperatures, the polymer is assumed to be a random copolymer and its T_g should follow the Fox equation.⁸ This effect has not been observed in the present research. At low temperatures, the main processes are propagation of the polymer backbone and branching. The T_g is therefore attributed to the chemical nature of the copolymer. Since DR is similar to BER in its chemical structure, the polymer formed is packed similarly, and increasing the content of BER is not expected to significantly change the T_g . Since XD has a different chemical structure, it was expected that the T_g will drop upon addition of BER. The effect of the addition of BER is hardly observed up to 55%. A similar trend is observed in systems containing MY. This implies that, in systems with different chemical structure of the epoxides, the glass transition at low temperatures of cure depends on the cure temperature itself, which determines the packing of segments rather than the contributions of the homopolymer segments.

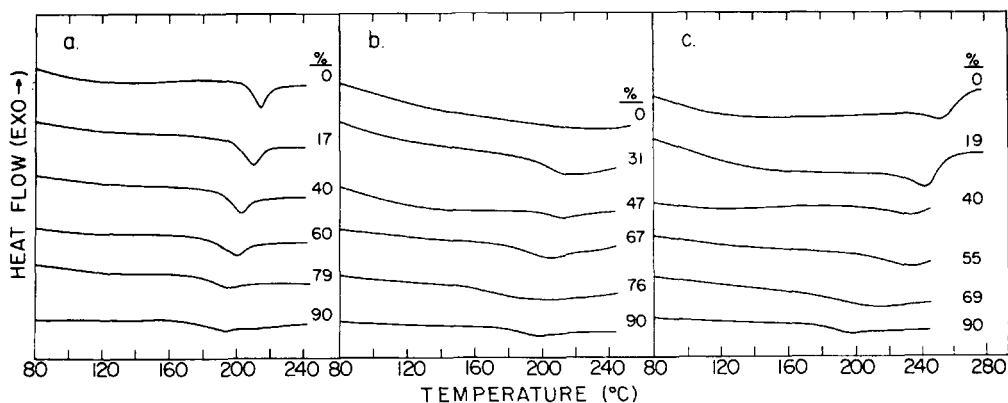


Fig. 3. Representative DSC scans of three epoxy systems cured at 175°C: (a) DR, (b) MY, (c) XD, with various BER contents.

The second transition indicates that, upon heating, the system continues to react. As a polymer cures, cross-linking, which restricts the motion of chain segments, occurs and results in an increased glass transition temperature. Representative DSC scans of samples cured at 175°C for 24 h are shown in Figure 3. Here, only one transition is observed. The higher the BER content, the lower is the T_g . That only one transition is observed is an indication that the system is homogeneous and the incorporation of BER is random. The transition also depends on the nature of the epoxy resins used. It decreases in the order T_g (XD) > T_g (MY) > T_g (DR), with larger differences at low concentrations of BER. These trends are shown in Figures 4, 5, and 6. It is also apparent that increasing the cure temperature results in increased T_g . Plots of T_g as a function of the cure temperature T_{cure} are shown in Figure 7.

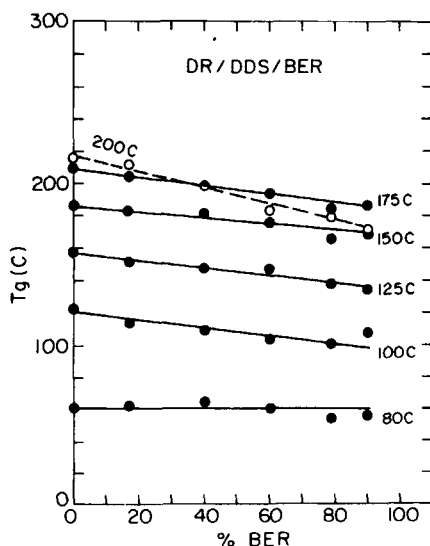


Fig. 4. Effect of cure temperature and BER content on T_g of systems containing DR.

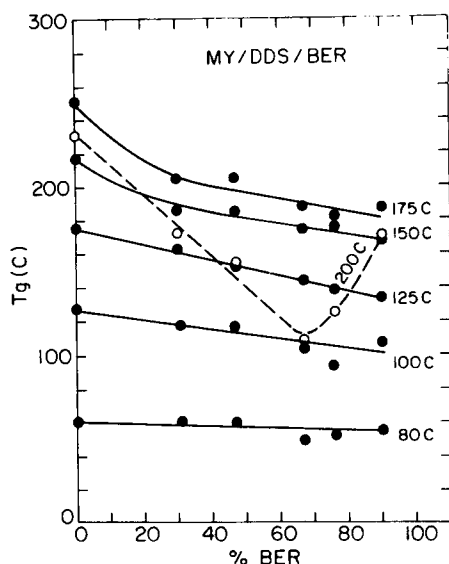


Fig. 5. Effect of cure temperature and BER content on T_g of systems containing MY.

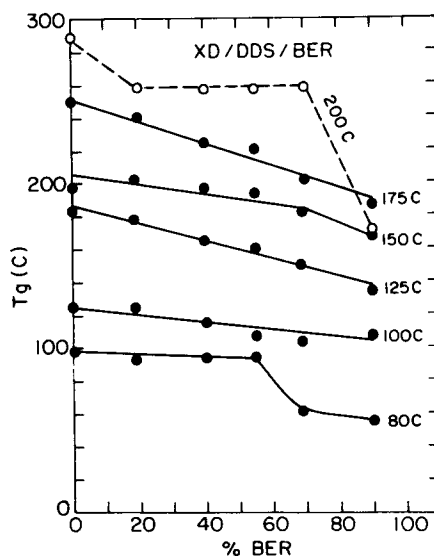


Fig. 6. Effect of cure temperature and BER content on T_g of systems containing XD.

However, if the cure temperature is too high (for example, 200°C), degradation may occur. The T_g measured at such temperatures may be lower than the theoretical T_g since the products of the degradation plasticize the polymer. The decrease in T_g may serve as a measure of the degree of degradation.

It was shown^{9,10} that the increase in the glass transition temperature in forming a cross-linked polymer is a combination of the change in the chemical nature of the copolymer that contributes $\Delta c T_g$ and of the formation of cross-links that contributes $\Delta r T_g$. Assuming that the two effects are indepen-

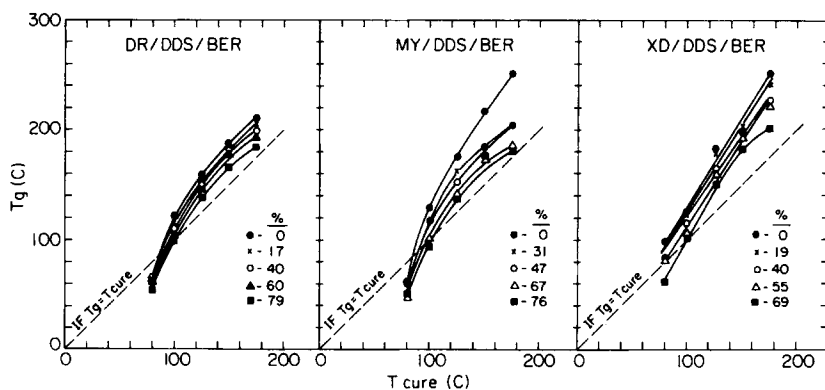


Fig. 7. T_g as a function of cure temperature T_{cure} : (a) DR, (b) MY, (c) XD.

dent of each other,

$$T_g = T_{g0} + \Delta c T_g + \Delta r T_g$$

where T_g is the glass transition temperature and T_{g0} is the initial transition temperature of the reaction mixture before polymerization.

It was found that $\Delta r T_g$ is related to the cross-link density $1/M_c$ by

$$\Delta r T_g = \frac{K}{M_c}$$

where $K = 39,000^{2,11}$ and M_c is the average molecular weight between cross-links:

$$M_c = \frac{\text{total weight of monomers}}{\text{total number of cross-links}}$$

Since the compositions are stoichiometric, and assuming that in a fully cured system all the functional groups have reacted, a theoretical M_c may be calculated for each system. If $T_{g\infty}$, the maximum glass transition temperature of the fully cured system, and T_{g0} are known, $\Delta c T_g$ may be calculated. T_{g0} was measured by cooling a mixture of the reactants to -130°C and scanning. The absence of a peak at -87°C (T_m of MEK) and at 82°C (T_b of MEK) indicates that the mixture is solvent free. $T_{g\infty}$ for DR-DDS was taken as 229°C ,² for XD-DDS as 352°C ,² and for MY-DDS as 251°C .¹² $T_{g\infty}$ for BER-DDS was determined as 186°C . Assuming random copolymerization, the theoretical $T_{g\infty}$ for systems containing BER was calculated according to the Fox equation.⁸

Table I represents the various glass transition temperatures and contributions by the chemical structure and by the cross-link density. Upon addition of BER, there is a slight increase in T_{g0} in systems containing DR and MY, but a decrease in systems containing XD. This is merely a reflection of the different chemical structure of the epoxides. The T_{g0} of all systems is roughly the same and thus contributes very little to the differences in the T_g of the cured systems. Increasing the content of the chain extender results in longer

TABLE I
Contributions of Chemical Structure and Cross-link Density to T_g^a

System	%BER (wt%)	$T_{g\infty}$	T_{g0}	M_c	$\Delta r T_g$	$\Delta c T_g$
DR-DDS	0	229	2	480	81	146
DR-BER-DDS	17	221	3	507	77	141
	40	211	5	549	71	135
	60	202	4	592	66	132
	79	194	5	639	61	128
XD-DDS	0	352	10	269	145	197
XD-BER-DDS	19	308	7	308	127	174
	40	265	6	367	106	153
	55	239	8	425	92	139
	69	216	7	497	78	131
MY-DDS	0	251	-3	187	209	45
MY-BER-DDS	31	227	2	249	157	68
	47	215	2	300	130	83
	67	201	2	404	97	102
	76	195	4	479	81	110
BER-DDS	90	186	2	669	58	126

^aAll temperatures are in °C.

segments and a decrease in cross-link density. Therefore, the contribution of cross-links to the T_g is smaller. The contribution of the chemical structure to the T_g also decreases with increased BER content in systems containing DR and XD. This effect is larger in systems containing XD since the chain extender significantly changes the chemical structure of the network; in systems containing DR, the only difference is the additional bromine atoms, which occupy a larger volume, making the spacings between chain segments larger. However, the basic chemical structure is unaffected owing to the similar backbones of DR and BER. A different trend is observed in systems containing the tetrafunctional epoxy resin MY. Here, because of the different structure of TGDDM itself, there are more cross-links inherent in the system; therefore, their contribution to the T_g is larger. However, increasing the content of the chain extender, which causes a decrease in T_g due to the decrease in cross-links, contributes to an increase by the change in the chemical structure of the network. This effect should be further investigated.

Kinetics of Cure

The kinetics of the cure reaction may be followed by monitoring the heat generated during the reaction. A representative dynamic DSC scan of a system containing DR and 17% BER is shown in Figure 8. The first peak is due to the heat generated by polymerization and the second, to degradation. These findings are in agreement with those found in the literature.¹³⁻¹⁵ It has been shown that at stoichiometric equivalent ratio of functional groups or excess of amine, the consecutive reaction of the epoxide groups with the hydrogen atoms of the amino groups is the only reaction that takes place. If the epoxide is in excess, or in the presence of compounds containing hydroxyl

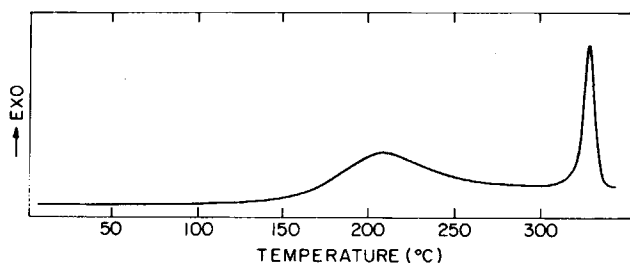


Fig. 8. DSC scan of DR-DDS with 17% BER.

groups or at high temperatures, etherification of the OH groups takes place. The latter is relevant to this study only at high temperatures, but at high temperatures, degradation occurs simultaneously. The kinetic parameters of the overall reaction between the amine and the epoxy groups may be calculated from the heat generated during a dynamic scan. We chose to measure the heat generated during a dynamic rather than during an isothermal scan since this has the advantage of a continuous heat generation, whereas in an isothermal scan, in addition to the initial heat needed to bring the sample to the test temperature, there is a residual heat¹⁶ when the reaction stops from being diffusion controlled as the viscosity rises and the mobility of the reacting ends is reduced.

Assuming that the heat generated in a dynamic scan is proportional to the extent of reaction,¹⁵ the reaction parameters may be calculated according to the kinetic equation

$$\frac{da}{dt} = k(1 - a)^n$$

where a is the degree of conversion, t is the reaction time, k is the overall rate constant, and n the overall reaction order. This equation precludes an induction period but for low temperatures or long times of reaction is a good approximation. It should be noted that this equation yields only apparent parameters because the reaction mechanism is complex and the reaction heats and the reactivities of functional groups in different resins are different. However, the results are significant as a general guideline and correlation among the systems investigated. Siegman and Narkis¹⁷ and Hartman and Lee¹⁸ have pointed out that the curing temperature and heating rate affect the reaction and the final structure of the cross-linked network. Therefore, a heating rate of 5°C/min was chosen as optimal. The kinetics parameters for the various systems are shown in Table II.

The heat generated in the polymerization reaction is similar in systems containing DR and XD but higher in systems containing MY. The heat of reaction of the neat systems is in agreement with published data.^{16,19} It was expected that the heat of reaction would be similar in all three systems since the oxirane ring is a glycidyl type in all three epoxy resins. However, although in DR and XD the glycidyl group is linked through an oxygen atom, in MY it is linked through a nitrogen atom. This is probably the reason for the different reactivity of the functional groups. The heat generated during the

TABLE II
Kinetics Parameters^a

System	%BER (wt%)	ΔH (J/g)	ΔH (KJ/mol eq)	n_{app}	$E\alpha_{app}$ (KJ/mol)	$\ln k_0$
DR-DDS	0	372.1	89.3	1.96	108.7	21.8
DR-BER-DDS	17	292.0	78.7	1.57	95.8	18.5
	40	223.6	73.6	1.11	79.6	14.2
	60	209.7	73.4	0.94	71.4	12.1
	79	95.2	48.9	0.83	71.2	12.0
	0	351.4	78.7	1.93	119.7	25.4
XD-BER-DDS	19	299.3	77.3	1.90	114.2	23.7
	40	241.1	75.3	1.88	105.9	21.5
	55	215.5	78.8	1.50	95.8	18.8
	69	142.0	61.5	1.05	78.9	14.2
MY-DDS	0	652.7	122.1	0.77	110.3	21.0
MY-BER-DDS	31	464.4	114.4	0.69	87.0	15.4
	47	380.1	111.6	0.75	84.0	14.8
	67	243.7	94.7	0.72	65.3	9.8
BER-DDS	90	73.0	44.3	0.77	65.9	10.6

^aRate: 5°C/min.

polymerization of BER and DDS is much lower and is probably a result of the stabilizing effect of the aromatic bromine. Therefore, increasing the content of BER in the system is expected to cause a decrease in the reaction heat. The apparent activation energy is also decreased with increased BER content. An interesting trend is observed in the apparent overall reaction order upon the addition of BER: it decreases from the theoretical $n = 2$ to about 1 in systems containing DR and XD but remains about 0.75 in systems containing MY. This is an indication of a different reaction mechanism. In neat DR-DDS and XD-DDS, the overall reaction order agrees well with the assumptions that the only reactions taking place are additions of primary and secondary amino groups to epoxy groups and that the ratio of reaction rate of the hydrogen atom in the primary and secondary amino group is independent of conversion.¹⁴ In systems containing MY and upon addition of BER, there are apparently simultaneous competing reactions that have yet to be investigated.

The overall parameters enable us to calculate the overall isothermal conversion as a function of time. The solution for the kinetic equation for $n \neq 1$ is

$$A = 1 - [kt(n - 1) + 1]^{1/(1-n)}$$

Calculated conversions as a function of reaction time for a system containing DR-BER-DDS with 17% BER, at 150, 175, and 200°C are shown in Figure 9. Calculated conversions at 175°C as a function of time for systems containing DR-DDS with various amounts of BER are shown in Figure 10. The time to reach 0.9 conversion for the various systems at 150, 175, and 200°C is shown in Table III. As seen from Figure 10 and Table III, the addition of BER results in faster reactions in all three epoxy systems. This may be explained by the higher reactivity of BER due to the longer chain and the polarity induced by

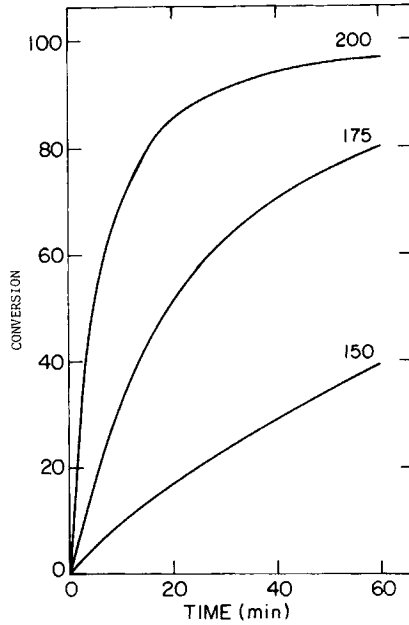


Fig. 9. Calculated conversion as a function of reaction time for DR-BER-DDS with 17% BER.

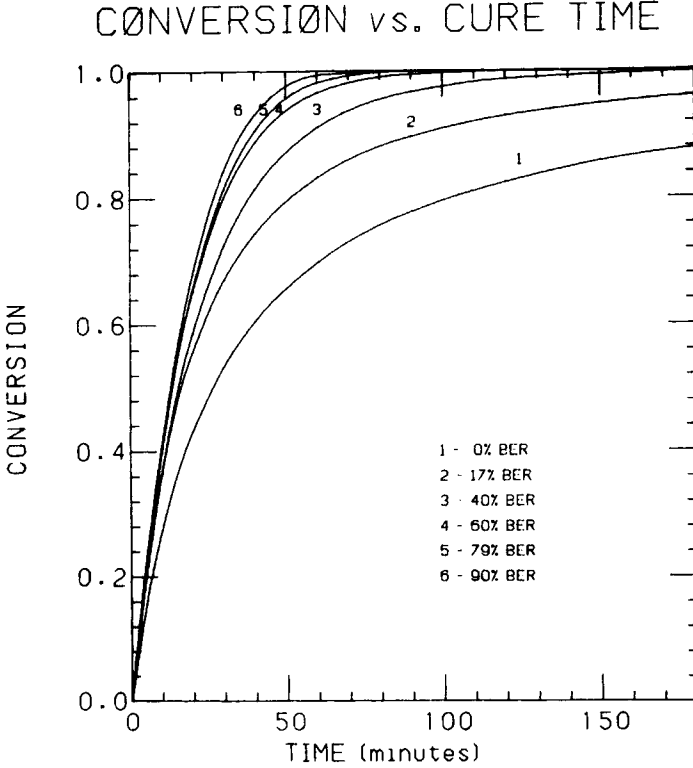


Fig. 10. Calculated conversion as a function of time for DR-BER-DDS systems.

TABLE III
Time to Reach 0.9 Conversion (min)

System	%BER	Temperature (°C)		
		150	175	200
DR-DDS	0	1282	225.9	48.4
	17	496.2	92.4	27.9
	40	200.3	56.7	18.4
	60	130.8	42.2	15.3
	79	120.7	39.3	14.2
XD-DDS	0	756.3	114.1	20.7
	19	829.5	135.5	26.8
	40	685.3	127.5	28.4
	55	333.7	73.0	18.7
	69	153.5	43.7	14.3
MY-DDS	0	942.8	163.7	34.2
	31	311.4	78.6	22.8
	47	258.2	67.7	20.6
	67	181.3	64.4	25.5
BER-DDS	90	102.0	35.8	14.1

the bromine atoms. Chain extension, which results in longer spacings between cross-links, apparently renders more flexibility to the systems; thus the rate of reaction is faster. Increasing the temperature also results in faster reactions, as expected.

The cured systems exhibit high thermal stability. No degradation has been observed in DSC experiments up to about 200°C. Thermogravimetric analysis shows that no major weight loss starts to occur up to about 270°C. The neat DR-DDS and XD-DDS systems, with peak temperatures T_{peak} of 416 and 412°C, respectively, are the most stable systems. The thermal stability is decreased upon the addition of BER, as is shown in Figure 11. However, the

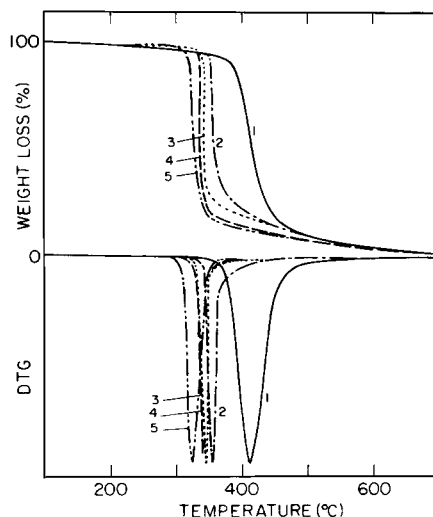


Fig. 11. TGA of systems containing XD-DDS with various BER content: (1) 0% BER; (2) 19% BER; (3) 40% BER; (4) 69% BER; (5) 90% BER.

TABLE IV
Thermogravimetric Analysis Data^a

Material	%BER (wt%)	T_{peak} (°C)
DR-DDS	0	416
DR-BER-DDS	17	354
	60	338
	79	334
XD-DDS	0	412
XD-BER-DDS	19	354
	40	342
	55	342
	69	342
MY-DDS	0	386
MY-BER-DDS	31	296
	67	296
	76	306
BER-DDS	90	328

^aRate: 20°C/min under nitrogen flow.

addition of BER results in an increase in the onset temperature and the degradation peak is sharper. The peak temperatures for the various systems are represented in Table IV.

CONCLUSIONS

In this research we studied the effects of the incorporation of brominated epoxy resins in thermosetting systems containing di-, tri-, and tetrafunctional epoxy resins. Addition of the chain extender results in lower glass transition temperatures. The T_g of the cured systems depends on the temperature of cure. The T_g of the cross-linked systems is the sum of the contributions of the chemical structure of the reacting compounds, the chemical nature of the polymer, and the density of the cross-links. It does not follow the order of functionality but rather the general trend T_g (tri) > T_g (tetra) > T_g (di). The overall reaction order of the reaction and activation energies decrease with increased BER content in systems containing DR and XD, but in systems containing MY the overall order of the reaction remains the same.

All systems are thermally stable, with peak degradation at about 300–400°C. However, the addition of BER, which imparts flame retardancy to the material, results in lower degradation temperatures.

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