Effect of Type of Substitution in 4,4'-Bis-(diaminodiphenyl) Methane Hardener on Cure Kinetics, Mechanical, and Flame Retardant Properties of Tetrafunctional Epoxy Resins

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ABSTRACT: The nature of the substituent in 4,4'-bis-(diaminodiphenyl) methane (DDM) hardener on the cure kinetics, mechanical, and flame retardant properties of N,N,N',N'-tetraglycidyl diaminodiphenyl methane (TGDDM) resin is investigated in comparison with unsubstituted DDM and widely used 4,4'-bis-(diaminodiphenyl) sulfone hardeners. Dynamic differential scanning calorimetry (DSC) and cure rheology studies showed that the substitution decreased the reactivity of the amine. An electron-withdrawing chlorine substituent was found to be more effective than an electron-releasing methyl group in reducing the amine reactivity. Substituted and unsubstituted DDM hardeners showed two peaks in their DSC thermograms that were due to steric hindrance in the former and deficiency of amine in the latter. Substitution showed its effect on the mechanical properties and glass-transition temperature. The flexural modulus was increased; however, the Izod impact and glass-transition temperature were decreased in substituted amine systems. The limiting oxygen index results showed higher flame retardancy in the chlorine substituted hardener system compared to other hardener systems that were studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 480–491, 2006

Key words: nature of substitution; cure kinetics; mechanical properties; flame retardancy

INTRODUCTION

In terms of both properties and end uses, epoxy resins are among the most versatile thermosetting plastics. Epoxy resins have applications in a wide variety of fields like adhesives, castings, surface coatings, electronic encapsulation, fiber-reinforced composites, and so forth. However, limited storage stability (shelf life) is one of their major drawbacks, being an essential requirement of epoxy-based formulations, especially when they are used as one-part systems. Epoxy-based prepregs are widely used in manufacturing of structural composites where sufficient tackiness and drape are essential requirements of a prepreg to obtain a quality composite that in turn depends on the quality of the prepreg. To avoid the advance of curing during storage, the prepreg should be stored below room temperature; for many commercially available resins, the recommended storage temperature for maximum shelf life is around −20°C.[1] The maintenance of such a low temperature adds extra cost. Thus, it is very important in terms of both cost and quality of the final product to prepare quality prepregs that can be stored at room temperature.

One of the important parameters that affects the shelf life of epoxy formulations is the reactivity of the hardener. There is a need for novel curing agents that can meet the above requirements in obtaining longer shelf lives and final properties.

There are numerous ways to improve the latency of one-part amine–epoxy systems. Dicyandiamide (DICY) is a popular latent curing agent,[2] and an epoxy/DICY mixture is virtually stable at room temperature. On heating, DICY decomposes at about 140°C and the resultant fragments react with resin to form a three-dimensional network. In fact, DICY does not dissolve completely in the resin. Hence, it is probable that the latency of this hardener lies mainly in the insolubility of the hardener, which is a physical rather than a chemical consideration. Substituted ureas[3] and chain extended ureas[4] are also used as latent curing agents for epoxy resin systems.

An excellent approach toward the development of latency in curing agents has been demonstrated by the

use of aminimide compounds.[5] The aminimide contains a ylide structure ($-N^{-}-N^{+}\equiv$), which is responsible for the latent properties of these compounds, and it is stable at room temperature. Among various types of aminimides,[6,7] it has been reported that acylaminimides, which are thermolized to produce isocyanates and tertiary amines,[8] are particularly useful in many cases.

Another way to improve latency is by blocking the lone pair of electrons by using transition metals. The formation of dative covalent bonds between the ligand's nitrogen atom and the transition metal ions acts to prevent the cure reaction (otherwise initiated by a lone pair of electrons undergoing a nucleophilic attack on the strained oxirane ring of the epoxy). It was shown that the ligands dissociate when a certain temperature (depending on the nature of the transition metal, ligand stereochemistry, and counterion) is reached, allowing the lone pair of electrons on the nitrogen atoms of free ligands to initiate the polymerization reactions.[9,10] The same technique was used to impart latent cure properties in imidazole initiators when mixed with epoxy resins.[11,12] Hamerton et al.[13] used a series of complexes incorporating diamine (o-phenylene diamine and 2-aminobenzyl amine) ligands and containing acetato and chloro salts of Ni(II) and Cu(II) incorporated into two commercial epoxy resins (MY721and MY750) to improve the latency of the system.

A simple way of improving the shelf life is by reducing the reactivity of amine by decreasing its basicity. Generally, aromatic amines are preferred to their aliphatic counterparts, because of their lower basicity. Sterically hindered amines such as 2,2'-diethyl-4,4'-methylene dianiline,[14] 4,4'-methylene-bis(2,6-diethyl aniline) (MDEA), and 4,4'-bis(3-chloro-2,6-diethyl aniline)[15] are shown to decrease the basicity of amine. In our previous articles[16,17] the work was carried out on chlorine-substituted 4,4'-bis-(diaminodiphenyl) methane with N,N,N',N'-tetraglycidyl diaminodiphenyl methane (DDM–TGDDM) systems to study the effect of chlorine substitution and its position on the reactivity of the hardener. We found that chlorine substitution reduces the reactivity of the amine (DDM) and it does so more effectively when substituted at the ortho position. In continuation of this, the present work is carried out on the effect of the nature of substitution on the reactivity of the amine. Two chemically different substituents are selected for this: one is an electron-withdrawing chlorine and the other is an electron-releasing methyl group. The substituent position is kept constant (ortho position) and the relative reactivities of substituted amines are evaluated using differential scanning calorimetry (DSC) cure kinetics, cure rheology in comparison with unsubstituted DDM, and the most widely used 4,4'-bis-(diaminodiphenyl) sulfone (DDS). The effect of these
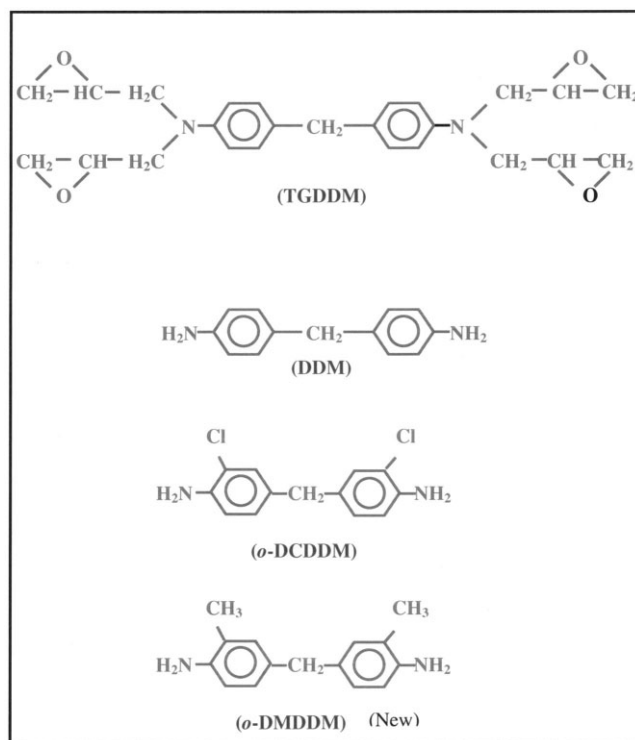
Figure 1 The structures of the resins and hardeners in the study.

substituents on the mechanical properties and flammability characteristics are also studied.

EXPERIMENTAL

Materials

DDM and DDS were procured from Fluka and used without further purification. o-Chloroaniline and o-toluidine (Loba Chemicals) were used after distillation. TGDDM and 3,3'-dichloro-4,4'diamino diphenylmethane (o-DCDDM) were synthesized according to the procedures reported in our previous articles.[16,17] The chemical structures of the resins and hardeners used in this study are shown in Figure 1.

Synthesis of 3,3'-dimethyl-4,4'diamino diphenylmethane (o-DMDDM)

The synthesis was carried out by modifying the procedure provided by Feedetova et al.[18] Distilled water (200 mL) was placed in a 1-L three-necked round-bottom flask fitted with a condenser. Then, 94 mL of concentrated hydrochloric acid was added under constant stirring. o-Toluidine (107 g) was added gradually to the above mixture while maintaining the temperature at 40°C, followed by dropwise addition of formalin (40.5 g, 37–41%, w/v) under constant stirring. The reaction was carried out at 55–60°C for 8 h under a

TABLE I
Details of Formulations

Formulation	Resin system	Composition (phr)
A	TGDDM + DDM	100:26.0
B	TGDDM + *o*-DCDDM	100:35.5
C	TGDDM + *o*-DMDDM (new)	100:30.5
D	TGDDM + DDS	100:33.0

nitrogen atmosphere. After completion of the reaction the contents of the flask were poured into a beaker and neutralized with (30%, w/v) aqueous sodium hydroxide solution. The product was washed several times with water, filtered, and then dried. The dried product was recrystallized from toluene.

The resulting yield of *o*-DMDDM was 50%. It was a white crystalline solid with a melting point of 158.5°C as determined by DSC. FTIR (KBr) $\tilde{\nu}_{max}$ (cm^{-1}): 3430 (NH$_2$, symmetric), 3348 (NH$_2$, asymmetric), 1621 (C=C, aromatic), 2910 (CH$_2$). ^{1}H-NMR (CDCl$_3$, δ): 2.0 (6H, s, CH$_3$), 3.54 (4H, s, 2NH$_2$), 4.58 (2H, s, CH$_2$), 6.5 (2H, d, 5,5'H), 6.7 (4H, *tri*, 2,2', and 6,6')

Preparation of cured neat resin casts

Resin (100 g) was placed in a beaker and heated in an oil bath. The amount of hardener according to the type of formulation shown in Table I was then added at 130°C (for DDM at 100°C) and mixed thoroughly until a clear solution was formed. Then, the resin formulation was pored into aluminum molds covered with Teflon coated glass fabric (tooltech tape to facilitate easy removal of cured sheet) and cured according to the cure schedules given in Table II.

Methods

Spectroscopy

FTIR spectra were recorded on a Bruker FTIR apparatus (model Vector 22) using KBr pellets with wavenumbers from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1}. Each spectrum was the average of 20 scans.

High-resolution ^{1}H-NMR spectra were recorded on Bruker AMX400 at room temperature in solution state using CDCl$_3$ as a solvent.

DSC

DSC studies were conducted on a DuPont TA 2100 DSC instrument. Dynamic DSC scans were conducted at 2, 5, 8, and 10°C/min heating rates in a temperature range of 50–300°C under a nitrogen atmosphere.

Rheological studies

The rheology of cure studies were carried out using a HAAKE Rheocard 600p. The experiment was carried out in isothermal mode. Approximately 90 g of resin formulation was poured into the cavity of the preheated sigma blade mixture and closed properly to prevent pressure losses. The speed of rotation of the sigma blades was set at 8 rpm, and the torque was observed as a function of time. Initial flight in the torque was considered as the gel time at the set temperature. The experiment was continued until the torque touched 90 Nm or the reaction time reached 120 min, whichever occurred first. The same experiment was carried out at different isothermal temperatures (110, 130, 150, and 170°C) for various resin formulations.

Dynamic mechanical analysis (DMA)

Dynamic mechanical tests for various cured epoxy specimens were conducted on a Dupont TA-983 DMA module. The specimen dimensions were 60 × 13 × 5.5 mm. The tests were performed from 50 to 300°C at a 5°C/min heating rate in resonance frequency mode.

Mechanical tests

The flexural tests were carried out on a universal testing machine according to ASTM D 790. The specimen dimensions were 130 × 13.5 × 5.5 mm, and the span length was 88 mm. The tests were carried out in three-point bending mode at a 2.35 mm/min rate of loading at room temperature.

TABLE II
Cure Schedules for Formulations

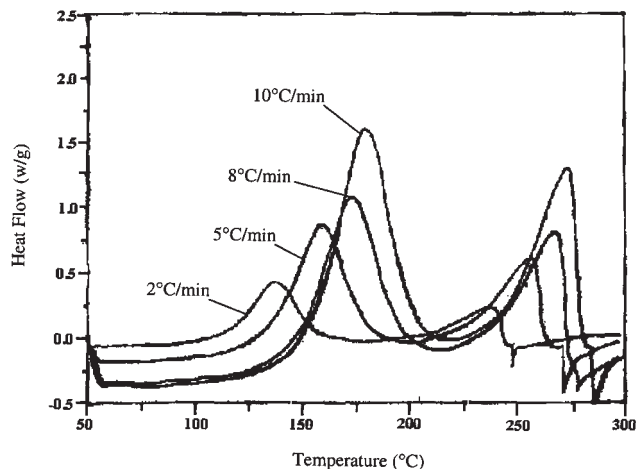| Formulation	Cure schedule	Postcure schedule
A	110, 120, 130, 140, 150, 160, 175, and 190°C for 1 h at each temperature	8 h at 200°C
B	130, 140, 150, 160, 170, 180, and 190°C for 1 h at each temperature	8 h at 200°C
C	120, 130, and 140°C for 1 h at each temperature 3 h at 150°C, 1 h at 175°C, and 1 h at 190°C	8 h at 200°C
D	130, 140, 150, 160, 175, and 190°C for 1 h at each temperature	8 h at 200°C

Figure 2 Common DSC thermograms of formulation A at different heating rates.

Izod impact tests were carried out according to ASTM D 256 on a CEAST impact tester. Unnotched specimens were used whose dimensions were 60 × 13 × 5.5 mm. The energy of the striking pendulum was 7.5 J, and all tests were conducted at room temperature.

Limiting oxygen index (LOI)

The tests were carried out according to ASTM D 2863 by using an Atlas LOI tester. The specimen dimen-sions were 100 × 6 × 3 mm, and they were clamped vertically at the center of the column. The flow valves were set to introduce the desired concentration of oxygen in the column. The entire top of the specimen was ignited with an ignition flame so that the speci-men was well ignited. The ratio of the concentration of oxygen to nitrogen was adjusted in such a way that the sample burned up to a 50-mm length in 3 min. The oxygen index was then calculated in terms of the following:

$$LOI = \frac{O_2}{O_2 + N_2}$$

where O_2 is the volume flow of oxygen at the deter-mined concentration and N_2 is the volume flow of nitrogen.

RESULTS AND DISCUSSION

Curing studies

The formulations studied in this work are shown in Table I. The weights of all hardeners are not same in these formulations. Generally, DDS is used at 27–35 phr, but in this study it was fixed at 33 phr. All other hardeners were taken in such a way that (considering their difference in molecular weights) the epoxy/
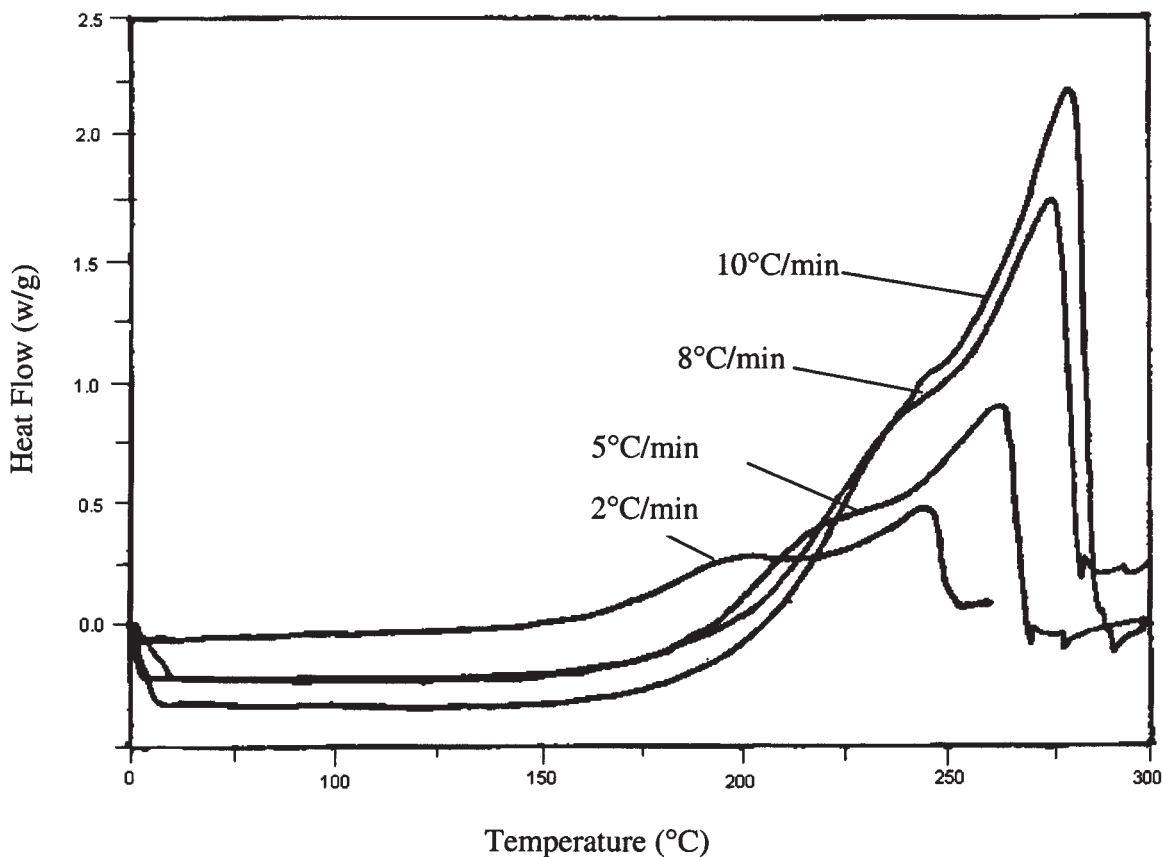

Figure 3 Common DSC thermograms of Formulation B at different heating rates.
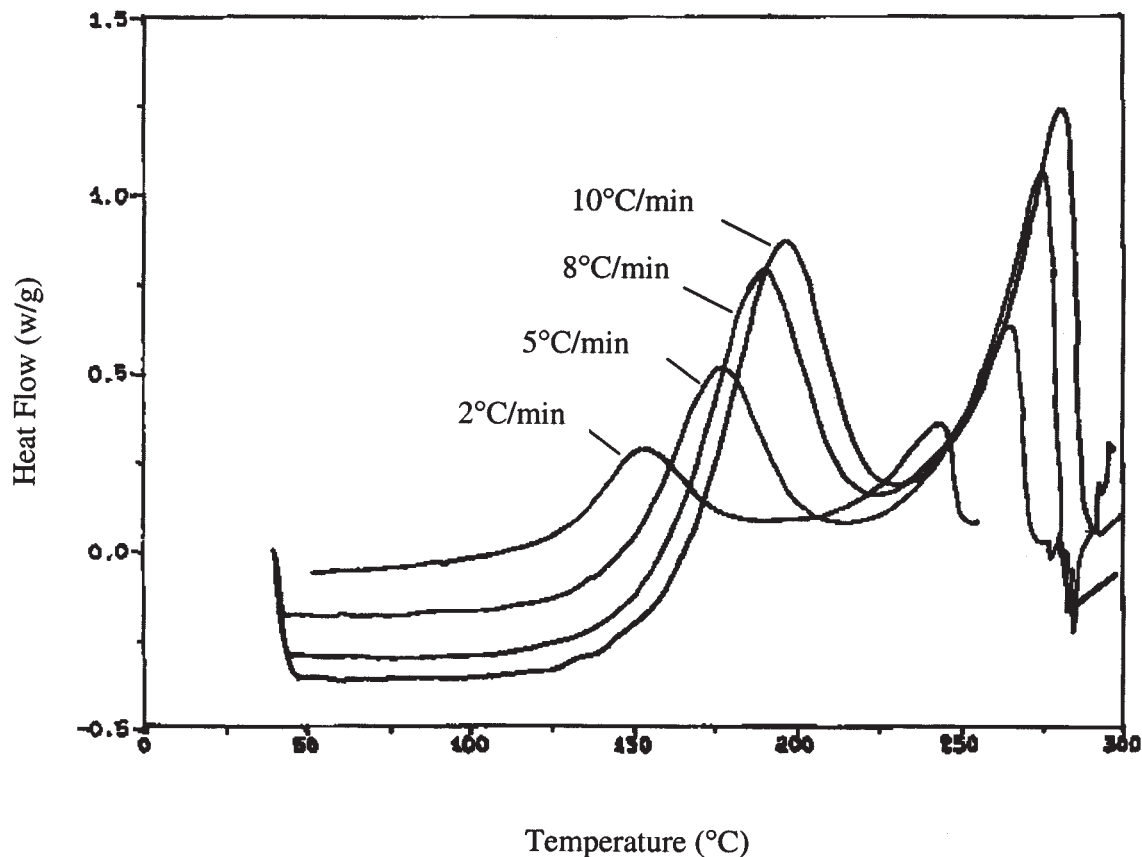
Figure 4 Common DSC thermograms of formulation C at different heating rates.

amine ratio in each case was equal to that of the epoxy–DDS system.

Curing studies by DSC

Figures 2–5 show the DSC scans at different heating rates for all formulations. From the Figure 6 we found that, except in the case of the DDS system (D), all other formulations showed two peaks. There are different reasons for the appearance of two peaks in different formulations. In the case of substituted amines (B and C), the reason for this is steric hindrance. Duffy and Hartmann[19] observed two peaks in DSC thermograms of hindered amine–epoxy systems. The steric hindrance exerted by substituent groups was more severe in the latter stages of the reaction, which further reduced the rate of the secondary amine–epoxy reaction. In the case of the DDM-based formulation (A), the two peaks are due to insufficient hardener quantity. This was confirmed by performing DSC runs of TGDDM formulations with different DDM hardener concentrations. As shown in Figure 7, the height of the second peak decreases with increasing concentration of DDM and finally at 40 phr the second peak apparently disappears. From these observations it can be explained that the first peak corresponds to primary

amine and secondary amine–epoxy reactions. There is no contribution from the amine–epoxy reaction to the second peak, because the second peak starts at around 200°C (at a 2°K/min heating rate), which is well above the temperature required for the secondary amine–epoxy reaction.[19] Moreover, the heat of reaction of first peak is almost twice that of the second peak and the height of the second peak is reduced as the amine concentration increases. The heat of reaction at 40 phr DDM (in which only one major peak was observed) is more or less equal to the total heat of reaction obtained for the formulations with the lower hardener concentrations. This indicated a complete reaction well below 200°C, which indicates the reaction is primarily between amine and epoxy.

In the case of the *o*-DCDDM formulation (B), two peaks were observed by DSC (Figs. 3, 6). Jagadeesh et al.[16] also observed two peaks in TGDDM/*m*-DCDDM systems. However, the two peaks observed in this case are not as well resolved as in DDM (A) and *o*-DM-DDM (C) formulations, even at a 2°K/min heating rate. This may be attributable to the increased electron-withdrawing inductive effect apart from the steric hindrance of substituted chlorine, which also decreases the primary amine reactivity to a greater extent; and, because of this, the cure reaction starts at
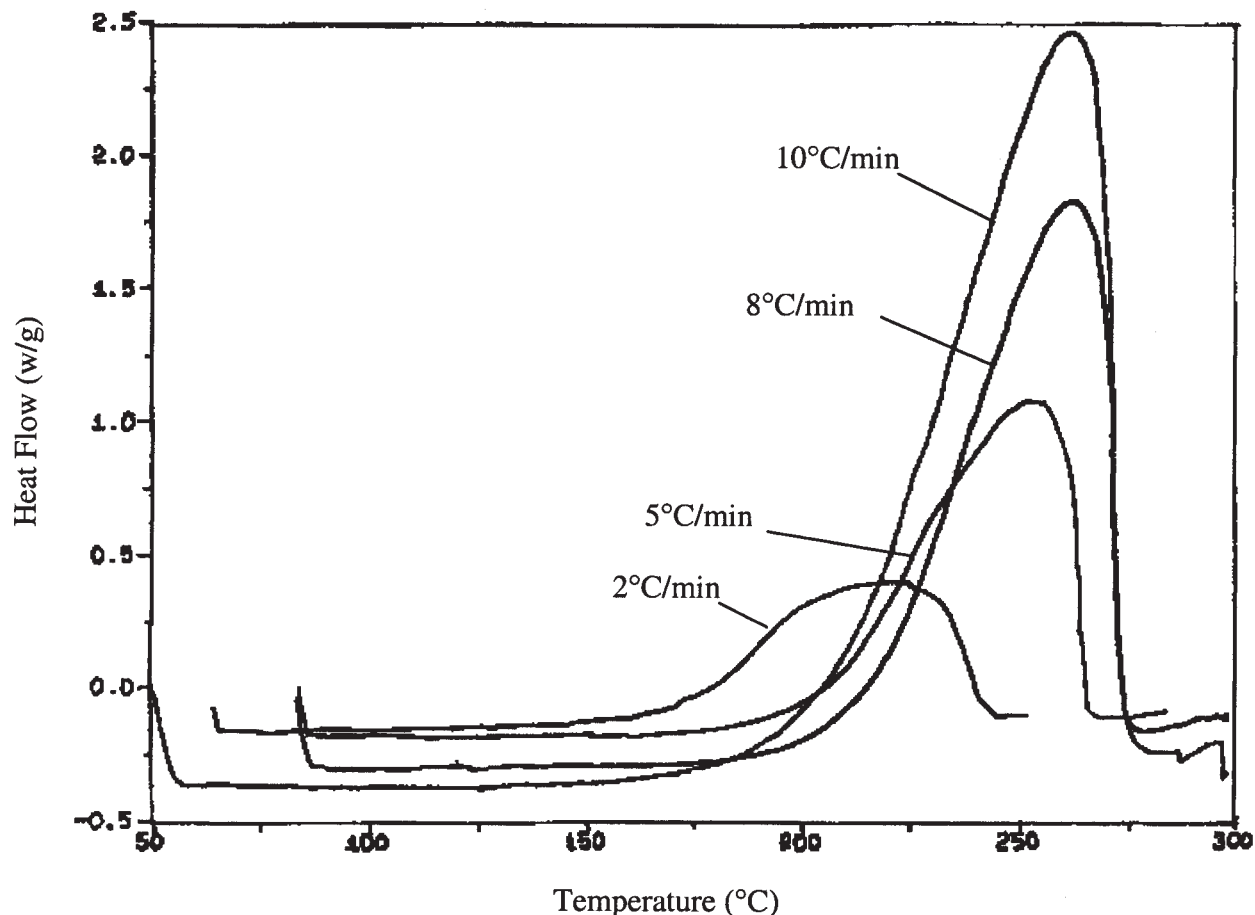
Figure 5 Common DSC thermograms of formulation D at different heating rates.

a higher temperature (at 142°C). Because the reaction starts at a higher temperature, before the primary amine–epoxy reaction is completed, the temperature reaches a point where epoxy–secondary amine/hydroxyl group reactions also start. Hence, these two reactions might have overlapped to some extent.

In the *o*-DMDDM-based formulation (C) two DSC peaks were also observed (Figs. 4, 6). The cure reaction starts at a relatively low temperature (at 95°C), but it is still about 7–8°C more compared to that of the DDM system. This enhancement in the initiation temperature may be attributed to the steric hindrance exerted by the substituted methyl group. Compared to a huge increment in the initiation temperature (by about 50°C) in the chlorosubstituted hardener system (B), the increment in the methylsubstituted hardener system (C) is much smaller (only 7–8°C). The reason lies in the chemical nature and weight of the substituent group. Chlorine is heavier than methyl and it is more importantly an electron-withdrawing group whereas methyl is an electron-donating group, which increases the basicity and hence the reactivity of amine. In *o*-DCDDM the steric hindrance and inductive effect of chlorine atoms works synergistically in reducing the

reactivity of amine, whereas in *o*-DMDDM the steric hindrance and inductive effect of the methyl group oppose each other as far as the effect on the reactivity of amine is concerned. The steric hindrance effect of the methyl group has probably edged the inductive effect, which is reflected in the increased cure initiation temperature compared to the unsubstituted DDM hardener. Girard-Reydet et al.[15] also showed that the reactivity of MDEA is lower compared to DDM and introduction of chlorine at the meta position further decreased the reactivity of MDEA. It is also reported in various standard organic textbooks that, irrespective of the inductive effect, the substituent at the ortho position reduces the basicity of amine, which is the so-called *ortho effect*.[20]

It is important to ascertain the reasons for the appearance of two peaks in the *o*-DMDDM system. Different reasons have been given in different formulations for the appearance of two peaks in DSC thermograms. In the chlorosubstituted system the appearance of two peaks were explained on the basis of steric hindrance exerted by chlorine atoms, whereas in the DDM hardener system the second peak was attributed to the epoxy–hydroxyl reaction due to deficiency in
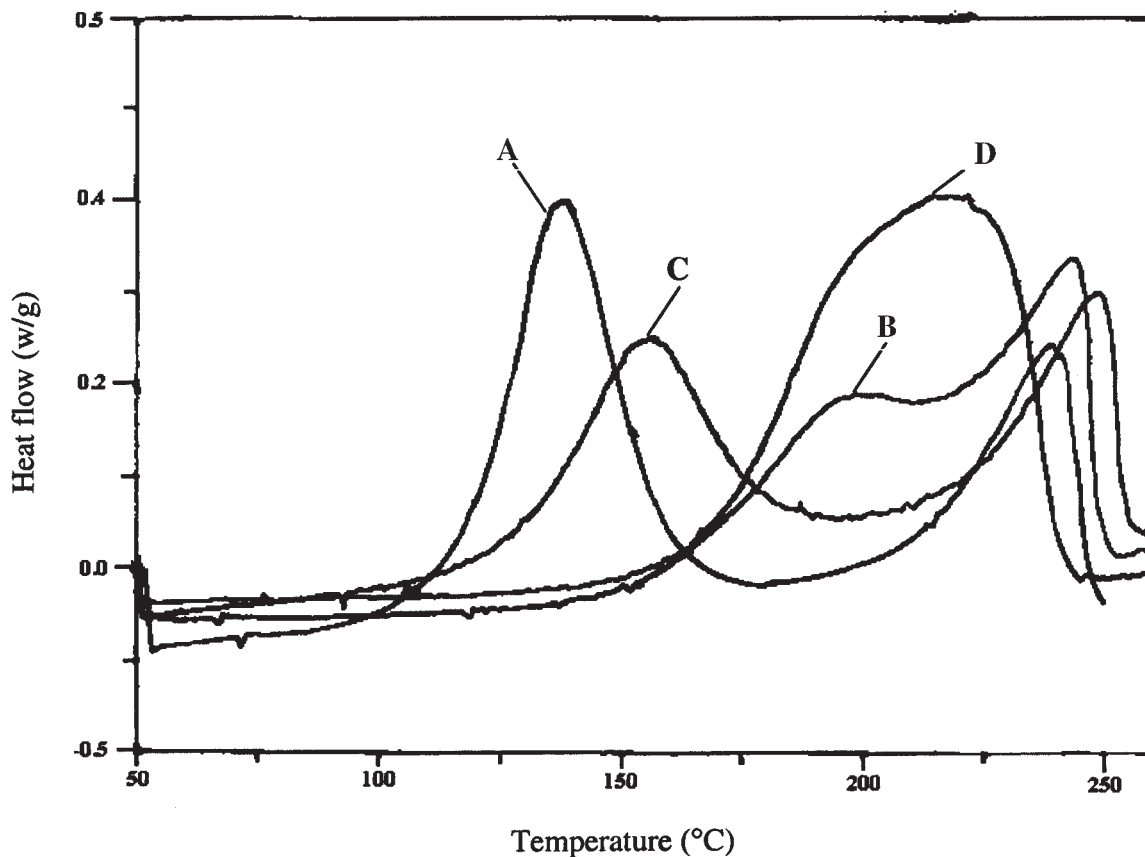
Figure 6   Common DSC thermograms of formulations A, B, C, and D at a 2°C/min heating rate.

the amine concentration. Unlike in the case of DDM, the difference in the heights of the two peaks is much smaller for the *o*-DMDDM system. The height of the second peak in the case of DDM is much smaller compared to the first one (the heats of reaction for the first and second peaks are 422 and 248 J/g, respectively). For *o*-DMDDM the height of the second peak is also small but the difference between the heights of the first and second peaks is much smaller. (The heats of reaction for the first and second peaks are 359 and 300 J/g, respectively.) Hence, in the DDM-based formulation the majority of the reaction corresponds to the first peak. In the *o*-DMDDM-based formulation the heights of the two peaks are more or less the same, indicating an appreciable amount of reaction distribution to both the peaks.

In case of DDM, the second peak starts at a much higher temperature (about 200°C), which is much higher for the epoxy–secondary amine reaction to take place and the difference in the temperature of completion of the first peak and initiation of the second peak is high (20°C). This indicates a very negligible reaction took place between these two temperatures. From the above observations it can be logically concluded that virtually no epoxy–amine reaction took place in the temperature range of the second peak. Thus, the sec-

ond peak can be attributed to the epoxy–hydroxyl reaction that is due to the presence of insufficient hardener. In the case of *o*-DMDDM, the second peak starts more or less at the same temperature (195°C) as in the case of DDM, but it starts immediately after the first peak is completed. Otherwise, it can be said that, before the reactions responsible for the first peak come to a halt, the reactions corresponding to the second peak begin. This means that the second peak is not exclusively due to the epoxy–hydroxyl reaction and the first peak is not exclusively due to the epoxy–primary amine reaction. Because the two peaks have comparable heats of reaction and based on the above reasons, it can be concluded that the first peak is attributable to primary amine and secondary amine–epoxy reactions, in which the former is predominant, and the second peak is due to secondary amine and hydroxyl–epoxy reactions, in which the latter is predominant. These conclusions were made exclusively on the basis of DSC studies of various formulations and need to be confirmed by other techniques like spectroscopy.

On the basis of the cure initiation temperature of *o*-DCDDM (142°C) and DDS (138°C), the conclusion can be drawn that the reactivity (basicity) of *o*-DC-DDM is marginally lower than DDS. However, examining the peak exothermic temperatures of *o*-DCDDM
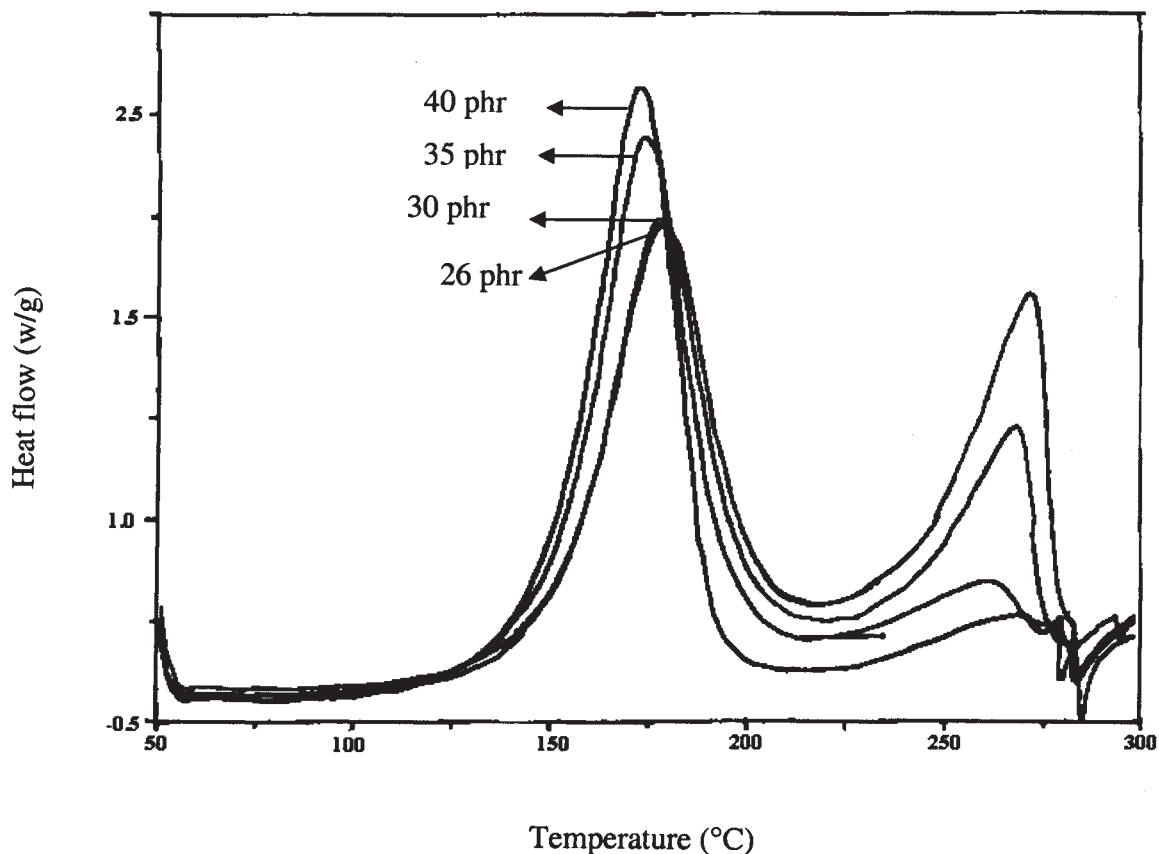
Figure 7 Common DSC thermograms of TGDDM + DDM formulations at different DDM concentrations.

(244°C) and DDS (221°C) suggests that the steric hindrance in the o-DCDDM system becomes more active as the reaction proceeds.

Cure rheology

Rheological changes that occurred during cure were monitored by using the sigma blade mixer on the HAAKE Rheocard. The results are shown in Figure 8. The gel time (the time at which initial flight in the torque is observed) is almost the same, but is slightly more (by 1 min) for the o-DCDDM system (28.8 min) compared to the DDS-based formulation (29.7 min) at 170°C. However, the difference in gel times increases as the temperature is reduced to 150°C [Fig. 8(a)]. After the gel time the cure reaction rate (slope of the curve) is also lower for the o-DCDDM system than for the DDS-based formulation. Even after 120 min, the o-DCDDM formulation reaches only 69.0-Nm torque whereas DDS touches 90 Nm within 104 min. The reason for the small difference in gel times at higher temperature (at 170°C) may be because both the primary and secondary amine/hydroxyl–epoxy reactions take place simultaneously at this temperature.[19] At 150°C, where the primary amine–epoxy reaction is more predominant, the higher gel time and slower

reaction rate after the gel time at this temperature suggests that the secondary amine–epoxy reaction in the o-DCDDM system is much slower than in the DDS-based formulation. Figure 8(a) shows that the gel time of the o-DMDDM system (C) at 150°C is smaller (7.68 min) compared to that of DDS (56.32 min) and o-DCDDM (65.92 min). This clearly shows that the reactivity of the o-DMDDM system is much higher than that of the o-DCDDM one. This result is exactly in accordance with the results obtained in the DSC studies. Figure 8(b) shows that the gel time of the o-DMDDM system at 130°C (26.88 min) is higher compared to that of the DDM (4.8 min) system (A) at the same temperature. The reactions were not carried out at 150°C for the DDM-based formulation and at 170°C for the o-DMDDM-based formulation because the material was charred because of the very high rate of release of heat (due to the higher reactivity of the hardener). Figure 8(c) shows that the gel time of o-DMDDM at 130°C is still 1.2 min higher compared to that of DDM-based formulation at 110°C. The above facts indicate the reduction in reactivity of DDM by methyl substitution.

DSC cure kinetics

Cure kinetic parameters were evaluated by using Ozawa and Kissinger equations and the results for the
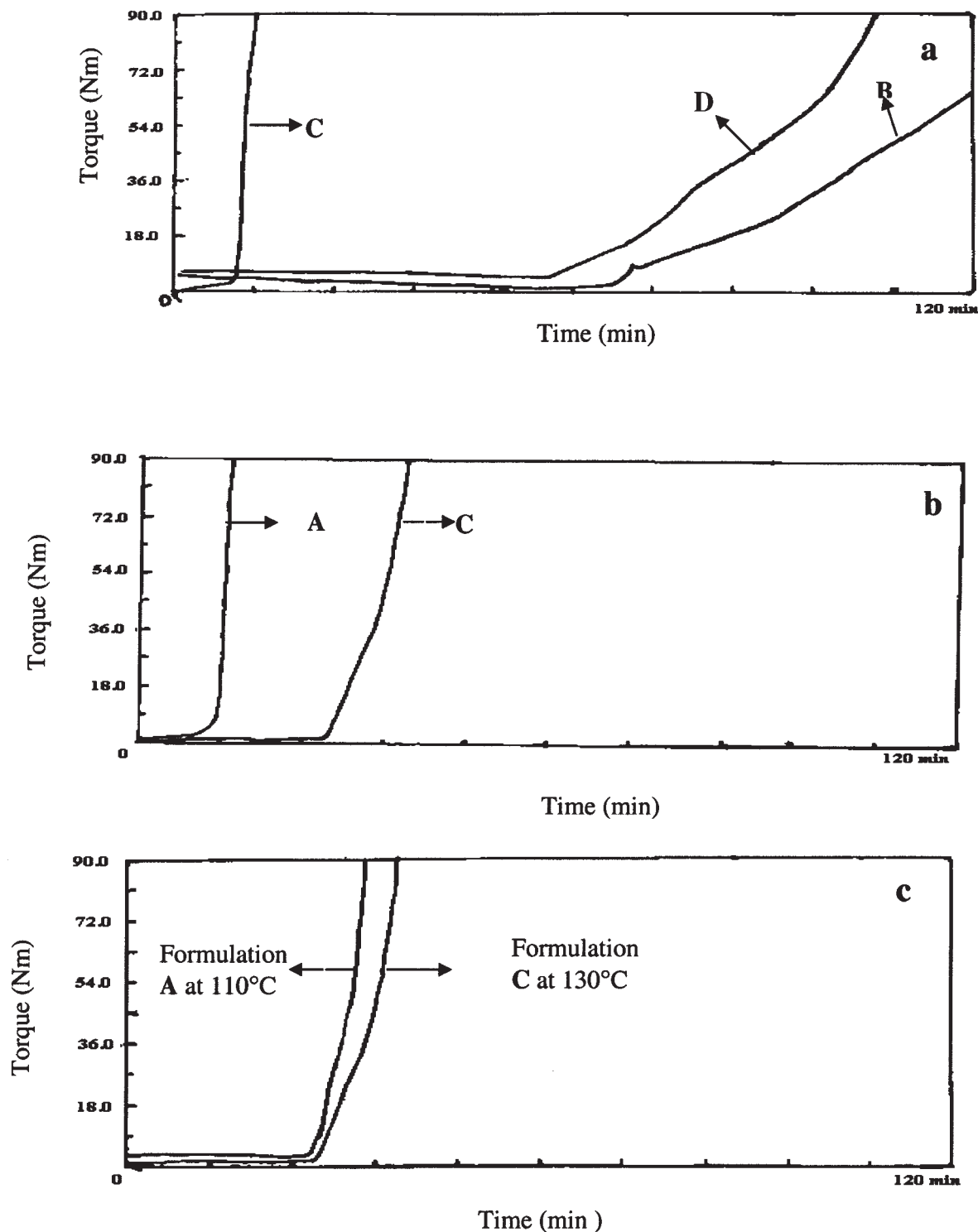
Figure 8 Torque versus time graphs for (a) formulations B, C, and D at 150°C; (b) formulations A and C at 130°C; and (c) formulation A at 110°C and formulation C at 130°C

formulations are presented in Table III. Good agreement of the kinetic parameters evaluated by different methods is observed. The activation energy corresponding to the first peak (E_{a1}) in the case of the two peak systems is lower than that of the second peak.

This is obvious because the rate of the primary amine–epoxy reaction is orders of magnitude higher than the secondary amine and hydroxyl group-epoxy reactions. The E_{a1} is the highest for the o-DCDDM system (B) and the lowest for DDM (A). The E_{a1} of o-DMDDM

TABLE III
Cure Kinetic Parameters of Various Epoxy Formulations

	Kinetic parameters					
	Activation energy (E_a) (kJ/mol)				Frequency factor (ln A) (min^{-1}) ln A_1	
	Ozawa		Rissinger			
Formulation	E_{a1}	E_{a2}	E_{a1}	E_{a2}	In	In
A	52.31	107.5	55.54	103.79	8.756	8.937
B	64.5	100.77	65.38	101.7	8.956	9.2522
C	54.44	93.98	60.0	96.82	8.7453	9.3122
D	76.98	—	85.36	—	8.643	—

(C) is found to be in between these two extremes, but the difference in E_{a1} for DDM and o-DMDDM is much lower than o-DMDDM and o-DCDDM systems (Kissinger). This corresponds to the explanation given earlier.

The activation energies for the second peak follow a different trend compared to that of the first peak. The activation energy corresponding to the second peak (E_{a2}) is highest for the DDM formulation, lowest for the o-DMDDM formulation, and in between these two extremes for the o-DCDDM formulation. The highest activation energy for the second peak of the DDM-based formulation further supports the fact that the second peak may be due to the slow epoxy–hydroxyl reaction. However, in the case of substituted hardener systems, the second peak is not exclusively due to the epoxy–hydroxyl reaction. The activation energy for o-DCDDM is higher than that of o-DMDDM, which is obviously due to the synergistic effect of the higher steric hindrance and electron-withdrawing inductive effect of the substituent chlorine atom. In the case of DDS, only one peak is observed and the activation energy lies in between the E_{a1} and E_{a2} of the two peak systems, which clearly demonstrates the overlap of epoxy–amine and hydroxyl group reactions.

Prediction of shelf life

The rheology of cure studies and DSC studies can be used to measure the relative reactivities of various aromatic amines. Substitution increased the cure initiation temperature (DSC) and gel times (rheology of cure). Moreover, the rate of reaction in the substituted amine was much slower than in the unsubstituted DDM hardener. Rheology studies also showed that the rate of reaction after the gel point of substituted systems was less compared to that of the unsubstituted DDM hardener. These results clearly indicated that the reactivities of the substituted hardeners were much lower than that of the unsubstituted DDM hardener; thus, higher shelf lives can be predicted for substituted amine systems. Among the substituted amine systems, the reactivity of chlorosubstituted

amine was much lower than that of methylsubstituted amine. Hence, a higher shelf life can be predicted with chlorosubstituted amine. The cure initiation and peak exothermic temperatures of the reaction of the o-DCDDM system were higher compared to that of the DDS hardener system. Therefore, a higher shelf life could also be predicted for the o-DCDDM-based system compared to the DDS-based one.

Mechanical properties

The results of the mechanical properties of all formulations in the study are summarized in Table IV. Marginal differences in the flexural strength and modulus among various formulations can be observed. However, a slightly higher strength and lower modulus are observed with the DDM-based formulation. These results suggest that the substitution increased the modulus and decreased the strength, which may be due to chain stiffening by substituent groups. The impact strength is highest for the DDM-based formulation and lowest for the DDS-based formulation. The substitution reduced the impact strength. These results clearly show that the reduction in chain mobility attributable to the bulky substituent group might have caused the reduction in the impact strength (because of reduced capability of heat dissipation through molecular mobility).

DMA

The DMA results are summarized in Table V. Figure 9 shows the DMA curves for all formulations. Note

TABLE IV
Mechanical Properties of Various Epoxy Formulations

Formulation	Flexural strength (MPa)	Flexural modulus (GPa)	Izod impact strength (kJ/m^2)
A	114	3.5	7.26
B	114	3.7	5.64
C	101	3.8	5.67
D	103	3.8	5.04

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