

New Tetrafunctional Epoxy Resin System with Increased Shelf Life

K. S. Jagadeesh, K. Shashikiran

JSSATE, C-20/1, Sector 62, Noida, U.P. India 201301

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ABSTRACT: Chlorine- and methyl-substituted aromatic diamines based on diaminodiphenylmethane were epoxidized and characterized. The effect of different substituents on epoxidation was studied. The cure studies of the two new tetrafunctional resins in comparison with unsubstituted resin *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) was carried out by DSC with 3,3'-dichloro-4,4'-diaminodiphenylmethane (*o*-DCDDM; 30% w/w) as a common curing agent. The mechanical properties such as flexural, Izod impact, heat distortion temperature (HDT), of such cured neat resins were also studied. The results of the cure studies indicate that the substitution of the α -hydrogen of the resin by chlorine or methyl group decreases the reactivity of the resin leading to an increase in the shelf life. This study also indicates that the functionality of the resin plays a pivotal role in the reactivity and thus the shelf life of an

epoxy resin system. The results of the mechanical properties of the neat resin casts obtained by subjecting to a common cure schedule when compared with the unsubstituted resin showed a decrease in impact strength, which is obvious because of the presence of a bulky pendant group but the impact strength was higher than that of the TGOS30 resin system. Results of flexural strength of the different substituted neat resin casts did not show much of a deviation from that of the unsubstituted resin system. The HDT results indicate no significant difference in the values of the unsubstituted resin vis-a-vis with substituted resin systems. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2790–2801, 2004

Key words: tetrafunctional epoxy resin; shelf life; cure kinetics

INTRODUCTION

The epoxy resins continue to dominate the high-performance composite applications as matrix resin mainly because of its good mechanical and thermal performance. One of the major drawbacks of epoxy resins are their low fracture toughness due to their highly crosslinked network. Efforts to improve the fracture toughness are continuing worldwide by addition of secondary rubber phase or an advanced thermoplastic phase such as poly(ether-imide) (PEI).^{1–2}

The overall toughness of the epoxy resins has thus been successfully improved, thereby continuing the usage of such type of resin system. The existing carbon/glass prepregs based on tetrafunctional epoxy matrix resin used in the aerospace industry lose their ductility³ or processibility in 2 months when stored at room temperature, and 1 year when stored at -18°C . Very few publications in the direction of improving shelf life were found.^{4–10} Based on the literature data, an effort was made in this article to improve the shelf

life of the epoxy resins by modifying the molecular structure of the matrix resin constituents.

EXPERIMENTAL

Materials

N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM; Reutapox) and epichlorohydrin (Trizma Chemicals, Japan) were used as such. *o*-Chloroaniline (Loba Chemicals, Bombay, India) and *o*-Toluidine (Loba Chemicals) were used after distillation. The synthesis of *o*-DCDDM was carried out according to the procedure followed in our previous article.¹¹

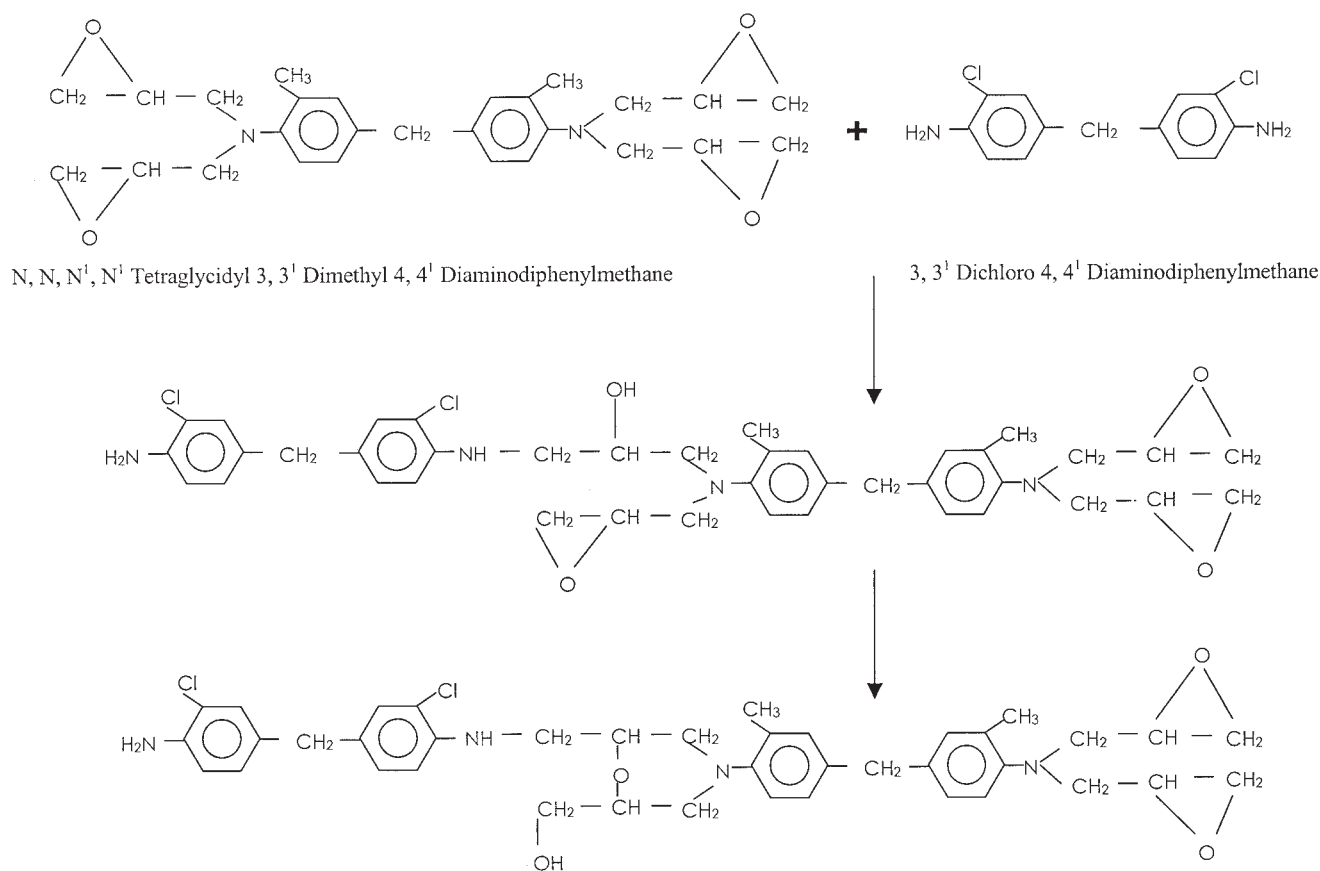
3,3'-Dichloro-4,4'-diaminodiphenylmethane (*o*-DMDDM) was synthesized as follows.

Synthesis of *o*-DMDDM

o-DMDDM was synthesized by modifying the procedure followed in the literature.¹²

In a round-bottomed flask fitted with a water-cooled condenser and a mechanical stirrer and heater, concentrated hydrochloric acid (90 mL) and water (200 mL) were taken with *o*-toluidine (107 g). After addition, the flask was cooled to room temperature and 40.5 mL formaldehyde was added without allowing the temperature to exceed 45°C .

Correspondence to: K. S. Jagadeesh (Kalpatarumysore@rediffmail.com).



Scheme 1 Epoxy-amide reaction.

The temperature was then raised to 65–70°C for 8 h. After this, the reactants were neutralized with aqueous sodium hydroxide (30% w/v) and the amine was filtered and dried. The product was crystallized in benzene to get crystals.

IR- γNH_2 -, 3400 cm^{-1} , - γCH_2 -, 2800 cm^{-1} . M.P., 150°C (lit. 155°C).

Synthesis of *N,N,N',N'*-tetraglycidyl-3,3'-dichloro-4,4'-diaminodiphenylmethane (TG-*o*-DCDDM)

Epichlorohydrin (1500 mL) was added to a three-necked R.B. flask fitted with a mechanical stirrer, condenser, and a nitrogen inlet through which nitrogen atmosphere was maintained throughout the reaction. The contents were then warmed to 70°C and *o*-DCDDM (100 g) was added. The temperature was then raised to 105°C with constant stirring for a period of 36 h. After this, the epichlorohydrin was stripped under vacuum, and the residual resin was dissolved in methanol, poured into the R.B. flask, and heated to 65°C. The above intermediate was neutralized by the dropwise addition of aqueous sodium hydroxide (30%w/v) with vigorous stirring for a period of 1 h. After addition, the contents were further stirred for half an hour. The remaining methanol and water were

stripped under vacuum; the residual resin was extracted in methyl ethyl ketone (MEK), washed with water, dried over anhydrous sodium sulfate, and the resin was stripped off under vacuum to remove MEK. The obtained resin was characterized as follows.

IR- γOH -, 3400–3600 cm^{-1} , - γEpoxy , 908–912 cm^{-1} . EEW = 140 g/mol (theoretical = 122.5 g/mol). Hydrolyzable chlorine < 0.8%.

Synthesis of TG-*o*-DMDDM

Epichlorohydrin (1500 mL) was added to a three-necked R.B. flask fitted with a mechanical stirrer, condenser, and a nitrogen inlet through which nitrogen atmosphere was maintained throughout the reaction. The contents were then warmed to 70°C and *o*-DMDDM (100 g) was added. Then, the temperature was raised to 85°C with constant stirring for a period of 20 h. After this, the epichlorohydrin was stripped under vacuum, and the residual resin was dissolved in methanol, poured into the R.B. flask, and heated to 65°C. The above intermediate was neutralized by the dropwise addition of aqueous sodium hydroxide (30% w/v) with vigorous stirring for a period of 1 h. After addition, the contents were further stirred for half an

TABLE I
Effect of Epichlorohydrin/Amine Ratio on Epoxidation of Different Diamines at 75°C for 8 h

Epichlorohydrin/ Amine ratio	EEW <i>o</i> -DCDDM resin	EEW <i>o</i> -DMDDM resin	EEW DDM resin
20/1	400 ^a	272–290	190–195
30/1	380	280–290	153–158
45/1	320	255–263	140

^a The resin cured on its own without addition of the curing agent within 48 h, indicating a very low epoxidation level.

hour, and the remaining methanol and water were stripped under vacuum; the residual resin was extracted in MEK, washed with water, and dried over anhydrous sodium sulfate. The resin was stripped off under vacuum to remove MEK. The obtained resin was characterized as follows.

EEW-135 g/mol (theoretical = 112.5 g/mol); color, transparent deep red. IR- γ OH-, 3400–3600 cm^{-1} , epoxy, 968–993 cm^{-1} (see Scheme 1).

Methods

The DSC studies were conducted on a TA DuPont 2100DSC instrument by adopting the method of variable peak exotherm to determine the kinetic parameters of different resin formulations. The dynamic scans were conducted at 5, 10, 15, and 20°C/min heating rate.

Gel time studies were conducted by inserting a probe into the resin formulations maintained in an oven for every 10-min interval. At higher temperatures, 170 and 180°C, the gel time studies were conducted in a similar manner but by maintaining the samples in an oil bath and by verifying cure for every 3 min.

The mechanical properties such as flexural and tensile strength were conducted on a Lloyd universal testing machine with a 100KN-load cell. The Izod impact test and heat distortion temperature (HDT) tests were conducted on CEAST impact tester and CEAST HDT/VICAT apparatus, respectively.

The rheological studies were carried on HAAKE 600p plasticorder mixer attachment at isothermal condition of 170°C with 9 rpm motor speed.

RESULTS AND DISCUSSION

The optimum conditions for the epoxidation of the substituted diamines were arrived at and the effect of various processing parameters similar to the temperature, amine : epichlorohydrin ratio, and duration of epoxidation are given in Table I.

Theoretically, for epoxidation of the diamines, the ratio of amine/epichlorohydrin of 1 : 4 is required. However, the epoxidation levels cannot be achieved with a stoichiometric ratio of the reactants. Jagadeesh et al.¹³ reported the synthesis of tetrafunctional epoxy resin based on diaminodiphenylmethane. Epoxidation of the diaminodiphenylmethane was carried out at 75°C for 5–6 h with methanol–water azeotropic mixture as a solvent along with an epichlorohydrin/amine ratio of 17 : 1. Verma and Choudhary¹⁴ synthesized tetrafunctional epoxy resin TGDDM with an epichlorohydrin : amine ratio of 30 : 1 without any solvent at 50°C for 3 h, and the epoxy resin obtained was reported to have a functionality of 3.4 (theoretical value, 4). Based on the above literature, the epoxidation of various resins was carried out at different epichlorohydrin/amine ratios and at different temperatures for different extents of time. Table I shows the effect of the epichlorohydrin/amine ratio on the ep-

TABLE II
Effect of Temperature on Epoxidation of Different Diamines with 1 : 45 Amine/Epichlorohydrin Ratio

Temperature (°C)/h	EEW of <i>o</i> -DCDDM resin	EEW of <i>o</i> -DMDDM resin	EEW of DDM resin
75/8 h	275	172–181	130
85/8 h	245–260	172–180	120–125
105/8 h	201–223	160–170	Not carried out
115/8 h	195–210	149	Not carried out
115 for 24 h	173	135–140	—
115 for 40 h	138–145	—	—

TABLE III
Mechanical Properties of the Different Formulations Obtained Under an Identical Cure Schedule of 135 C/1 h, 145 C/1 h, 165 C/1 h, 175 C/1 h, 190 C/4 h

Properties	A	B	C	D
	TGDC DDM+ <i>o</i> -DCDDM (30%)	TGDMDDM+ <i>o</i> -DCDDM (30%)	TGDDM+ <i>o</i> -DCDDM (30%)	TGDDM+ DDS (30%)
Tensile strength (MPa)	35 (1.2) ^a	46 (2.66)	50 (1.2)	55 (1.7)
Tensile modulus (GPa)	2.0 (0.12)	3 (0.3)	3.9 (0.2)	4 (0.4)
Flexural strength(MPa)	77 (3)	102 (5.33)	107 (2.5)	145 (7)
Elongation (%)	4.5 (2)	4.91 (2.1)	3.44 (1.66)	3.7 (1.3)
HDT (°C)	181 (2)	192 (2)	200 (5)	219 (5)
Izod impact(J/M)	75 (2.34)	91 (3.7)	117 (4.2)	69 (2)

^a The values in the parentheses are the standard deviations for the respective values.

oxidation of the different diamines. The results from the Table I indicate that the epoxidation of an ortho-substituted amine is difficult when compared to an unsubstituted diamine. This is quite popularly known as the ortho effect. It can also be concluded from the results that better epoxidation levels can be achieved by maintaining higher reaction temperature, which also means a supply of the desired activation energy for the sterically hindered systems (as shown in Table II). It can be further learned from the results that carrying out epoxidation at very high epichlorohydrin/amine ratios also leads to an increase in the probability of the collision of amine and epichlorohydrin molecules, thereby leading to higher epoxidation.

If the results of the epoxidation of two sterically hindered diamines, namely *o*-DCDDM and *o*-DMDDM, are compared, it is found that the epoxidation of chlorine-substituted system is found to be more difficult than the methyl-substituted diamine. Chlorine renders the amine less basic as it withdraws the lone pair of electrons, which is essential for the epoxidation. The basicity of the amines was noted down from the data published in the Merck Index for the dissociation constant of the amines.

From the table, it is evident that the epoxidation of chloro-substituted amine is difficult when compared to the epoxidation of methyl-substituted amine, which is further difficult when compared to the unsubstituted resin. These facts are further supported by the dissociation constants of various amines available in the literature.

The different epoxy formulations used in this study are shown in Table III. Gel time studies were conducted for different epoxy resins with *o*-DCDDM (30%) as a common curing agents at 130, 140, 150, 160, 170, and 180°C in comparison with the existing TGDDM+diaminodiphenyl sulfone (DDS) (30%) formulation (DDS; Gharda Chemicals, Baroda, India). The results are tabulated in Table IV. Results indicated that the resin system comprising the methyl-substituted resin gelled after a longer time when compared to the other resin system. The presence of impurities similar to hydroxyl groups due to incomplete dehydrohalogenation is reported to accelerate the cure process,¹³ which also means to decrease shelf life, and an uptake of moisture by the prepregs would facilitate cure and decrease shelf life.

The results of the mechanical properties of the cured neat resin casts obtained of the above formulations are given in Table III.

Because the cure behavior of epoxy systems greatly influences the mechanical properties, it is important to understand and interpret the cure behavior.

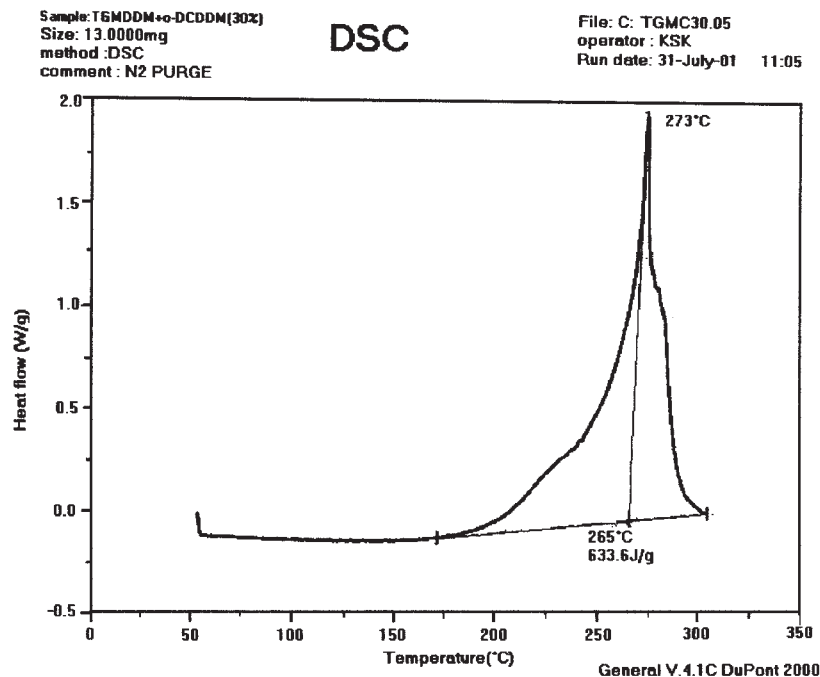
DSC studies

The DSC studies were conducted for all the above formulations at 2, 5, 10, and 15°C/min heating rate. The kinetic parameters, namely the activation energy and the frequency factor, were calculated on variable peak exotherm methods. The equations of Ozawa (1)

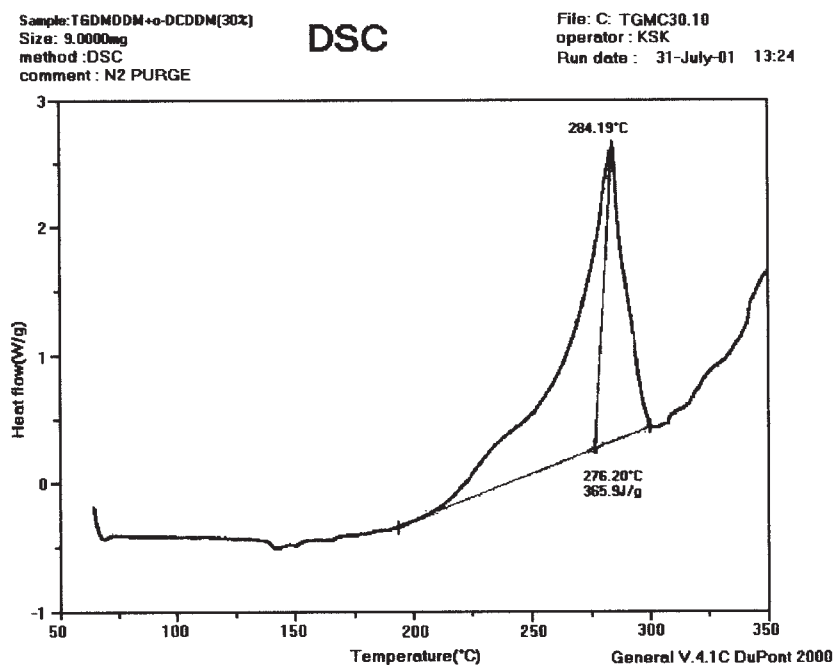
TABLE IV
Effect of Postcure on the Mechanical Properties of Various Formulations

Postcure time/temperature	A		B		C		D	
	HDT (°C)	Tensile strength (MPa)	HDT (°C)	Tensile strength (MPa)	HDT (°C)	Tensile strength (MPa)	HDT (°C)	Tensile strength (MPa)
190°C/6 h	210 (2) ^a	40 (1.9)	212 (4)	46 (3)	208 (1)	48 (2.7)	225 (3)	56 (2.3)
190°C/9 h	215 (4)	42 (3)	212 (4)	48 (5.5)	210 (3)	45 (2)	230 (2)	55 (5)

^a Values in parentheses are the standard deviation values.



(a)



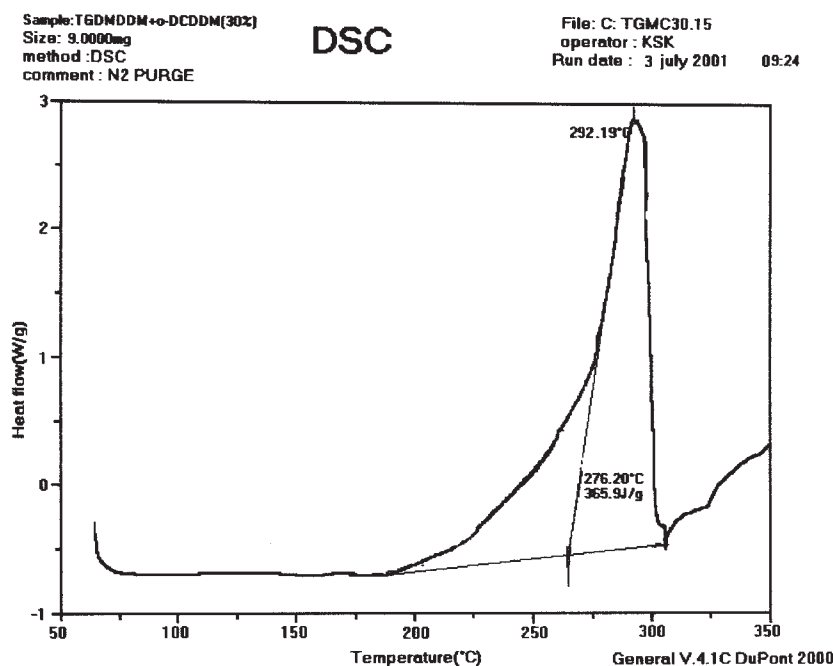
(b)

Figure 1 (a) DSC scan of Formulation B at 5°C/min heating rate. (b) DSC scan of Formulation B at 10°C/min heating rate. (c) DSC scan of Formulation B at 15°C/min heating rate. (d) DSC scan of Formulation B at 20°C/min heating rate. (e) DSC scan of Formulation A at 10°C/min heating rate. (f) DSC scan of Formulation C at 10°C/min heating rate. (g) DSC scan of Formulation D at 10°C/min heating rate.

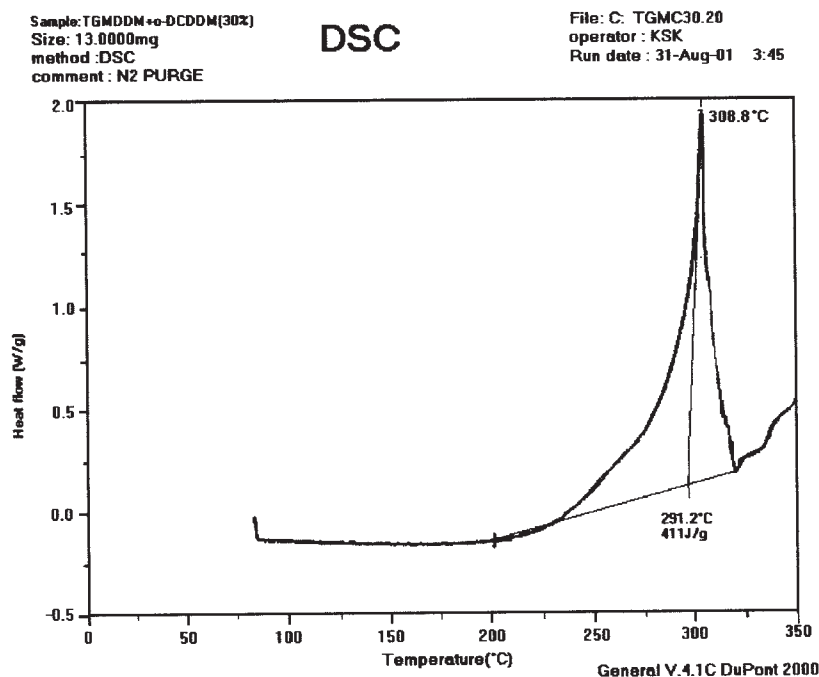
and Kissinger (2) were considered for calculating the kinetic parameters and are given below.

Figure 1(a–g) shows the Dynamic DSC thermograms of all the formulations at 10°C/min heating rate. From the graph, it is to be noted that the initiation

temperature (T_i) for the Formulation D is lowest, followed by Formulation C. Formulation A has the highest cure initiation temperature. This difference is due to the effect of the different types of groups present in the resin and the curing agents. Formulation D, con-



(c)



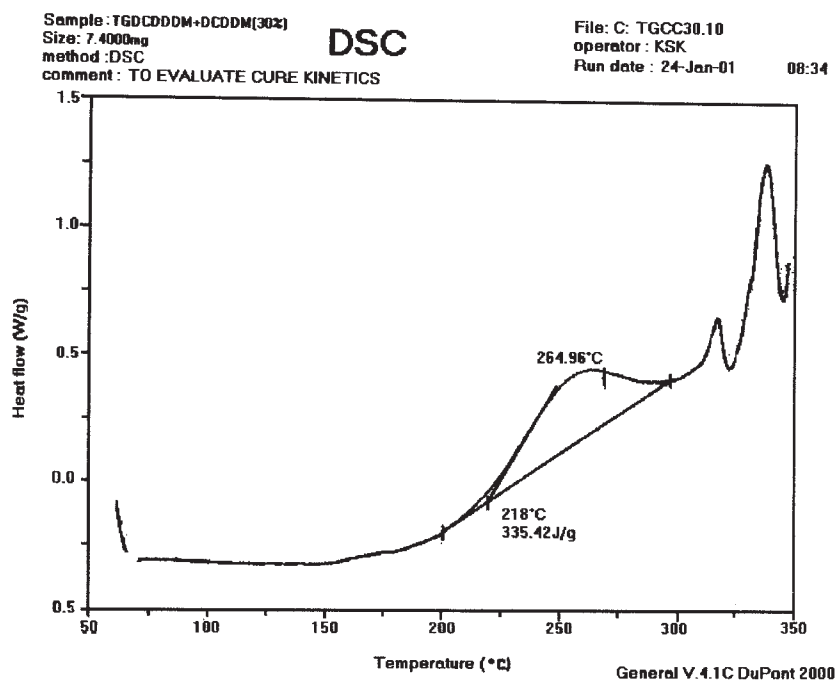
(d)

Figure 1 (Continued from the previous page)

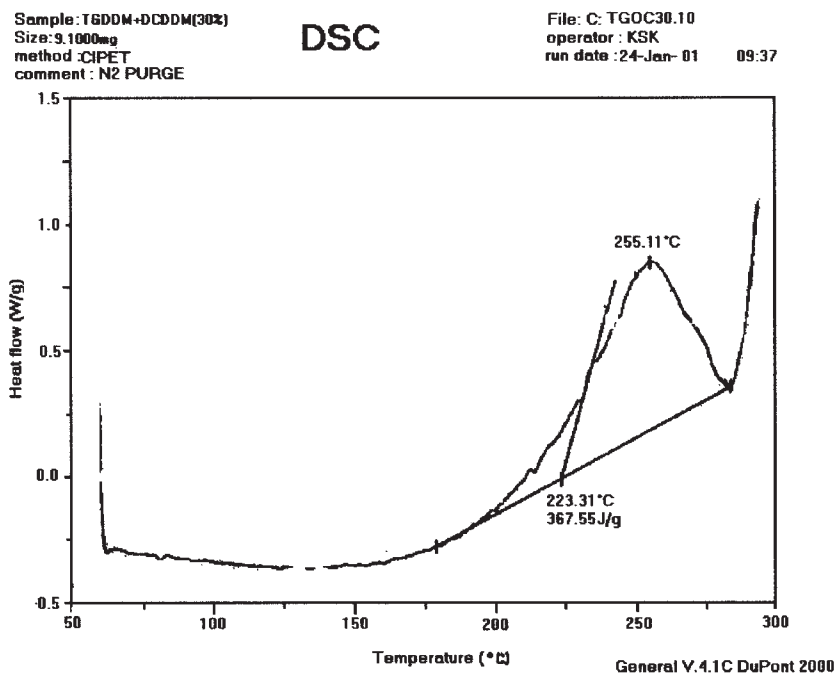
sisting of the unsubstituted resin TGDDM and DDS as curing agent, is a highly reactive formulation. TGDDM resin contains a higher functionality (3.6), has low free hydroxyl group, and does not contain groups, which reduces the reactivity of the resin. Also to be noted is the fact that DDS curing agent is more reactive than *o*-DCDDM curing agent, which was con-

cluded in our previous publication.¹¹ Formulation B, consisting of the chloro-substituted resin and *o*-DCDDM curing agent, is the next reactive system, followed closely by Formulation C.

B has low functionality (3.4), indicating a higher residual amine, and also has higher free hydroxyl groups. The residual amine easily reacts with the



(e)



(f)

Figure 1 (Continued from the previous page)

neighboring epoxy group and increases the concentration of —OH groups. Hydroxyl groups facilitate the cure process; hence, the chloro-substituted epoxy resin initiates at a lower temperature. Theoretically, chloro resin should show higher cure retardancy when compared to the unsubstituted system for a given curing

agent. This can only be possible if the functionality of the chloro- and unsubstituted resins are comparably the same. If these conditions prevail, then the chloro resin with steric hindrance would reduce the reactivity of the resin to a greater extent when compared to the unhindered TGDDM system.

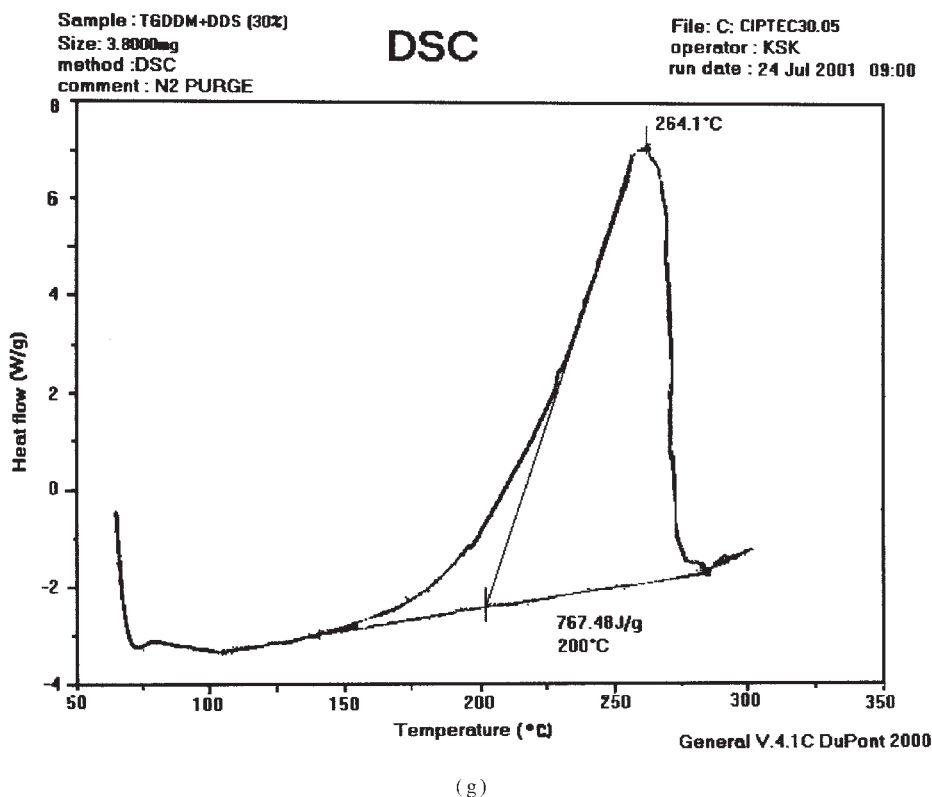


Figure 1 (Continued from the previous page)

Formulation A, having the highest shelf life, further emphasizes the above point. The methyl resin present in this system has a higher functionality of 3.6 when compared to the functionality of the chloro resin. The resin also contains ortho-substituted methyl group, which, due to its steric hindrance, reduces the reactivity of the resin. These two facts are the reasons for the high initiation and peak exotherm temperature of this formulation.

Rheological studies

Rheological studies of all the above formulations were carried out at an isothermal temperature of 170°C. The study was carried out by correlating torque versus time at a given temperature.

Figure 2(a–d) shows the graphs of time versus torque obtained for the four formulations.

From the graphs, it can be concluded that Formulation D is having the lowest time-of-torque-flight (ToTf) of 23 min. This is mainly due to the high reactivity of the DDS curing agent as concluded by DSC studies. Formulations B and C showed values of 36 and 38 min, which can be considered as almost the same. Formulation A has the highest time of 52 min. These data emphasize the same fact as revealed by the DSC studies.

The second considerable result from the Rheo graphs is the varying reactivity of different resin systems after the ToTf. Each resin system has its own path of torque increment from the initiation point. If we consider the time required for a resin system to reach a torque of 100 Nm from the torque initiation point, then the resin system showing the shortest duration of time to reach this torque value is Formulation D (reproducing the torque to 100 Nm). Formulation B requires a long time to achieve the same value. This is followed by Formulation A having the second highest value of time to reach the given torque. A has greater reactivity or decreased resistivity-for-cure in the vitrification region when compared to B. This is mainly due to the bulky chloro group, which requires higher energy for mobility and reaction when compared to the relatively lighter methyl-substituted resin system.

The results of the rheological studies for Formulation B indicate that the cure reaction is highly retarded in the vitrification region.

The results of the mechanical properties of various formulations are vivid and give the following indications.

Tensile strength and modulus of Formulation A is low, which is an indication of low-crosslink density formed in the matrix because of the low reactivity of the resin and the curing agent. A low Izod impact

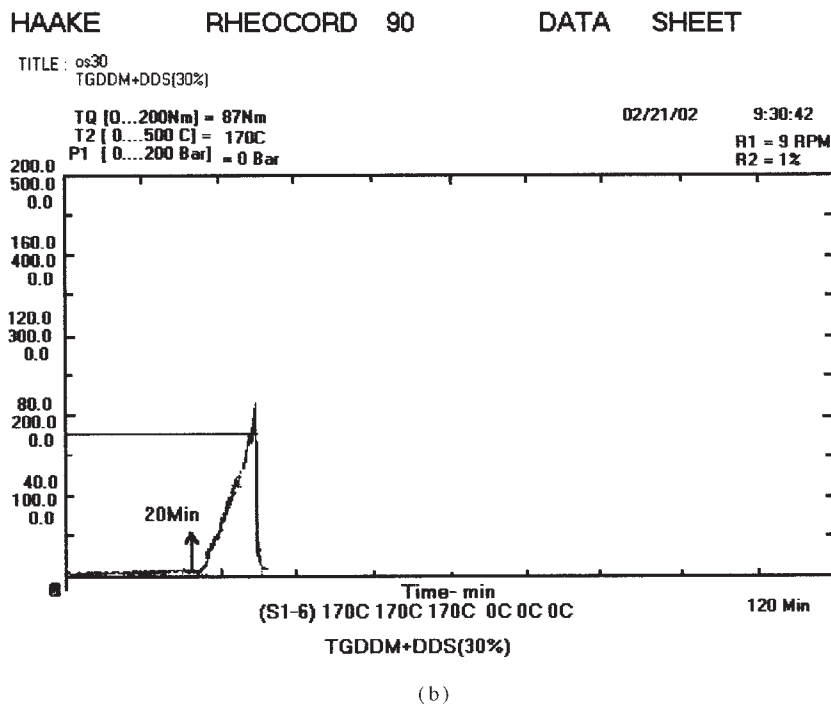
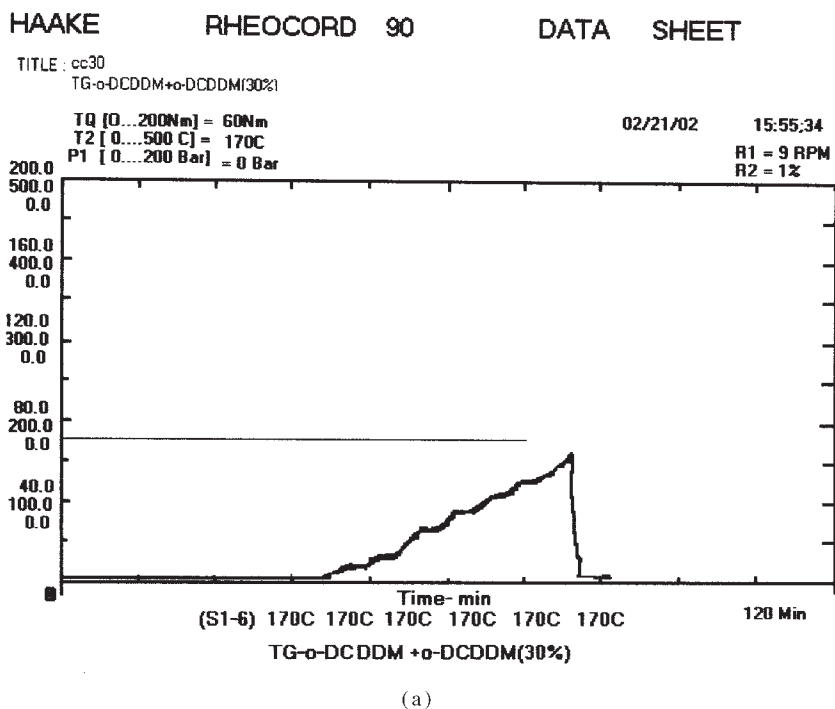
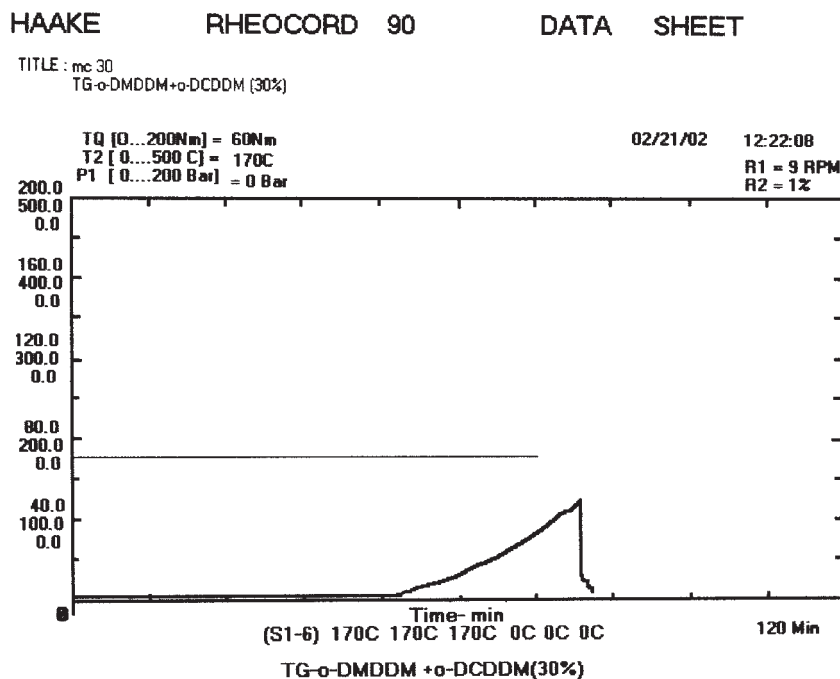


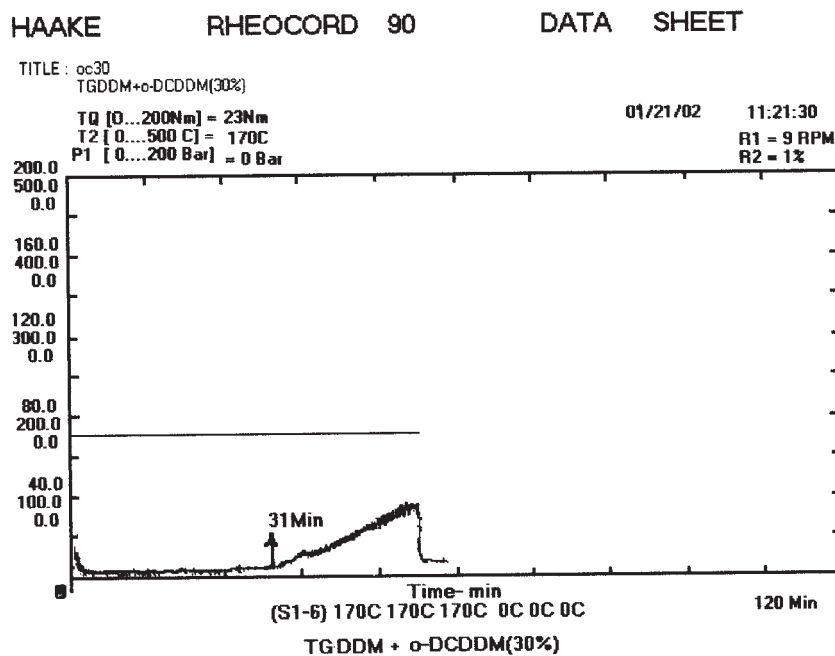
Figure 2 (a) Rheology graph of Formulation A. (b) Rheology graph of Formulation D. (c) Rheology graph of Formulation B. (d) Rheology graph of Formulation C.

strength despite a low crosslink density of this formulation indicates that heavy pendant chlorine atom in the amine as well as resin leads to a highly brittle matrix system. It is to be further realized from the result that the low molecular weight of the polymer is formed because of insufficient curing of Formulation

A, which led to low impact strength. In the case of Formulation B, the properties are found to be better when compared to the previous system. The formulation is having higher crosslink density when compared to Formulation A and hence has a higher tensile strength. This is due to the fact that the resin is having



(c)



(d)

Figure 2 (Continued from the previous page)

methyl group as the substituent, which is lighter than the chlorine atom; this allows for a greater extent of cure in the vitrification region, thereby increasing the crosslink density and in turn the mechanical properties. In the case of Formulation C, the tensile strength is much better for the same reason as said in the previous

case. The unsubstituted resin with a substituted chloro hardener would cure to a greater extent when compared to the curing of substituted resins with the same curing agent. The tensile strength of Formulation D is highest of all the systems. Formulation D consists of DDS as the curing agent. The sulfone group is polar and hence will

enhance the secondary forces between the microneetworks, thereby increasing the structural strength. Another point to be noted is that the reactivity of the DDS curing agent is higher than compared to the *o*-DCDDM curing agent. This leads to higher molecular weight and crosslink density for a given cure schedule.

Tensile modulus is much dependent on the molecular weight and crosslink density of a material. The results of the tensile modulus follow the same trend for different formulations. The same reasons discussed above hold equally well for the respective formulations.

HDT studies conducted on the four formulations do not show a notable deviation. The small changes found can be attributed to the effect of secondary forces and difference in crosslink density. In the case of Formulation **A**, the HDT is low for a neat resin cured at a particular cure schedule. This is due to the fact that the chlorine atom adversely retards the reaction during the vitrification region, thereby reducing the crosslink density.

Formulation **B** shows higher HDT when compared to Formulation **A**. Formulation **C** shows similar HDT as Formulation **B**. This is due to the fact that there is less steric hindrance in this case when compared to the previous two formulations. The resin in this case is TGDDM. Formulation **D** has the highest HDT of all the formulations. The trend is similar in the results of the tensile strength. This Formulation **D** has a higher crosslink density, and strong secondary forces between the micro networks, leading to high-dimensional stability.

Table V shows the effect of the postcuring time on the HDT and tensile strength of the various formulations.

From the results obtained as given above, it is clear that Formulations **A**, **B**, and **C** showed an increase in the HDT and mechanical properties due to the increase in the postcure time at 190°C from 3 to 6 h. This indicates that there was some residual reaction that could not occur due to the retarded reactivity of the three resin systems. In the case of Formulation **D**, the increase in the mechanical and HDT properties were not significant.

The results of the impact strength of all the formulations are given in Table IV.

Formulation **D** has the lowest impact strength when compared to other formulations. This is mainly because of the fact that this formulation has the highest crosslink density of all (as known by the HDT studies), which renders the system highly brittle. Despite a low-crosslink density, Formulation **A** has the second lowest impact strength of all. This, as said before, is due to the heavy pendant chlorine atom present in the epoxy resin. Formulation **B** and **C** have almost similar impact strength. Formulation **B**, due to the methyl group substitution, ends up with a lower crosslink density, thereby nullifying the effect of pendant group substitution.

CONCLUSION

Epoxidation of ortho-, chloro-, and methyl-substituted diamines based on diaminodiphenylmethane was successfully carried out. Epoxidation of ortho-, chloro-substituted diamine was found to be most difficult of all the diamines. The *o*-DMDDM amine was found to be relatively easier to epoxidize when compared to the chloro-substituted diamine but was relatively difficult than the epoxidation of diaminodiphenylmethane.

DSC curing studies were carried out for the three types of tetrafunctional resins with *o*-DCDDM as a common curing agent at 30% w/w. The studies revealed the effect of amine structure and functionality on the reactivity of the epoxy system. Ortho-, methyl-substituted resin showed delay in curing with a high activation energy followed by chloro-substituted resin and TGDDM resin system.

Rheological studies were carried out to determine the effect of structure of constituent on curing in the vitrification region. The ToTf of formulation with methyl-substituted resin showed the longest gel point followed by the chloro- and unsubstituted system. Further rheological studies also revealed that the rate of cure was drastically held up in the case of the heavy pendant chloro resin. Cure hindrance was least in the case of the conventional unsubstituted resin with *o*-DCDDM curing agent.

Mechanical properties of the substituted resin systems were found to be decreased when compared to the unsubstituted resin system. Mechanical properties were lowest for the resin system containing chloro-substituted resin and curing agent. Mechanical properties of the resin system with unsubstituted resin and chloro-substituted diamine were found to be the best.

Hence, substitution at ortho position is desirable in shelf life point of view but will decrease the reactivity of the system in vitrification region, thereby reducing the crosslink density, and in turn, reducing the mechanical properties of the resin system.

A resin system with ortho-, methyl-substituted resin and chloro-substituted diamine was ideal in terms of shelf life and mechanical properties.

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