

Effect of Chlorine Substitution in 4,4'-Diaminodiphenylmethane Hardener on Shelf Life and Mechanical Properties of Epoxies

K. S. JAGADEESH, J. GURURAJARAO, K. SHASHIKIRAN, SARVOTTAM Y. AMBEKAR

Central Institute of Plastics Engineering and Technology, Mysore 570016, India

Received 16 January 2001; accepted 8 May 2001

ABSTRACT: Curing of *N,N,N',N'*-tetraglycidyl-diaminodiphenylmethane with new curing agents like 3,3'-dichloro-4,4'-diaminodiphenylmethane and 2,2'-dichloro-4,4'-diaminodiphenylmethane in comparison with diaminodiphenylmethane and 4,4'-diaminodiphenylsulphone (DDS) was carried out using dynamic differential scanning calorimetry. The shelf life of various epoxy formulations was evaluated by the residual cure exotherm method. The glass-transition temperatures of cured epoxy formulations were determined using dynamic mechanical analysis. The mechanical properties such as the tensile strength, tensile modulus, flexural strength, and Izod impact strength were also evaluated and compared. The activation energy, frequency factor, and shelf life of chloro-substituted hardener formulations were high as compared to those of unsubstituted hardener formulations. The marginal differences in the glass-transition temperature, tensile strength, tensile modulus, and flexural strength and the small decrement in the Izod impact strength values were interpreted in terms of chlorine substitution.
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Key words: hardener substitution; shelf life; cure kinetics; mechanical properties

INTRODUCTION

Wide applications of amine cured epoxy resins in the fabrication of high performance composite materials has led to tremendous research interest in the cure and properties of resins.¹ The majority of the research work described in the literature deals with composites prepared from *N,N,N',N'*-tetraglycidyl-diaminodiphenylmethane (TGDDM) as an epoxy resin and DDS as a hardener.² However, intrinsic brittleness and lower shelf life con-

tinue to be drawbacks of these materials. A higher shelf life is doubtlessly desirable for the resin, so it may be noted that it increases with a decrease in the basicity of the curing agent. In the aryl amines it is known that introduction of chlorine into the ring decreases the basicity. In view of this, we thought of studying the effect of chlorine substitution in the hardener moiety for the shelf life of various formulations of TGDDM in the form of using 3,3'-dichloro-4,4'-diaminodiphenylmethane (*o*-DCDDM) and 2,2'-dichloro-4,4'-diaminodiphenylmethane (*m*-DCDDM) as hardeners. In order to have a comparative study, DDS and DDM hardeners were used and studied along with the above. Evaluation of the mechanical properties like the tensile, flexural, and Izod impact strengths of various formulations were undertaken in this study.

Correspondence to: K. S. Jagadeesh.

Contract grant sponsor: U.S. Office of Naval Research, Naval Research Laboratory; contract grant number: N00014-97-1-0998.

Journal of Applied Polymer Science, Vol. 83, 3082–3088 (2002)
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Table I Details of Various Formulations of Epoxy Resin

Formulation	Resin System	Composition	Amine/Epoxy Molar Ratio
A	TGDDM + <i>o</i> -DCDDM	100 : 20	0.3030
B	TGDDM + <i>m</i> -DCDDM	100 : 20	0.3030
C	TGDDM + DDS	100 : 20	0.33
D	TGDDM + DDM	100 : 20	0.43

EXPERIMENTAL

Materials

Epichlorohydrin (Trizma Chemicals), DDM (Fluka), and DDS (Fluka) were used as received. *m*-DCDDM was synthesized by following the procedure described in our previous article.³ *o*-DCDDM was synthesized from *o*-chloroaniline, and TGDDM was prepared by modifying the literature method.⁴

Synthesis of *o*-DCDDM

Into a round-bottom flask fitted with a water cooled condenser was poured distilled water (200 mL) to which concentrated sulfuric acid (57 mL) was added. 2-Chloroaniline (100 g) was gradually added to the above solution while maintaining the temperature at 45°C, followed by the dropwise addition of formalin (33 mL, 40% w/v) with constant stirring. After the addition was complete the flask was warmed to 85°C and maintained at that temperature for 12 h. After 12 h the contents were cooled to room temperature and neutralized with aqueous sodium hydroxide (30% w/v). The resulting solid was separated by filtration, washed with water, dried, and crystallized from chloroform. The product with a melting point of 105°C was characterized as follows: IR: γ_{NH_2} , 3400 cm^{-1} ; $\gamma_{\text{C}=\text{C}}$, 1610 cm^{-1} . NMR (CDCl_3 , δ): 6.37 (2H, d, 5,5'—H), 7.0 (4H, 2,2' and 6,6', —H), 3.8 (2H, s, —CH₃), 3.65 (4H, s, —NH₂).

Synthesis of TGDDM

Epichlorohydrin (1200 mL) was placed into a 2-L three-necked flask fitted with a condenser and a nitrogen inlet. The flask was warmed to 70°C, and then DDM (100 g) was added. The temperature was maintained at 75°C for 9–10 h. After 10 h the epichlorohydrin was stripped under reduced pressure, the resulting viscous product was dissolved in methanol (300 mL), and the contents were

warmed to 55°C followed by dropwise addition of (40% w/v) aqueous sodium hydroxide over a period of 1 h. The contents were further stirred for 0.5 h. Methanol was stripped off and the product was extracted in methyl ethyl ketone (MEK), washed with water several times followed by washing with hot water, and dried over anhydrous sodium sulfate. The MEK was stripped off to get the pure resin (128 g/mol epoxy equivalent weight; 1.1% hydrolysable chlorine; IR: γ_{OH} , 3600 cm^{-1} , epoxide = 908 cm^{-1} ; 17,000 cps viscosity at 50°C).

Methods

Differential scanning calorimetry (DSC) studies were conducted on a DuPont TA 2100 DSC instrument by adopting the method of the variable peak exotherm to determine the kinetic parameters of different resin formulations. The dynamic scans were conducted at 2, 5, 10, and 15°C/min heating rates.

Dynamic mechanical analysis (DMA) studies were carried out on a DuPont TA-983 DMA module in the temperature range of 30–250°C at a heating rate of 5°C/min. The specimens used were of 60 × 10 × 6 mm dimension.

The tensile and flexural strengths were examined on a Lloyds universal testing machine, and the Izod impact strength was determined by a CEAST impact tester according to ASTM standards. The tensile strengths of the specimens were determined at a 5 mm/min crosshead speed. The formulations employed in this study are given in Table I.

Curing Procedure

The respective hardeners (20 phr each) were added to the resin and heated to 100°C, and the contents were stirred for 15 min. A clear solution of the resin formulation thus obtained was poured into aluminum molds that were previously coated

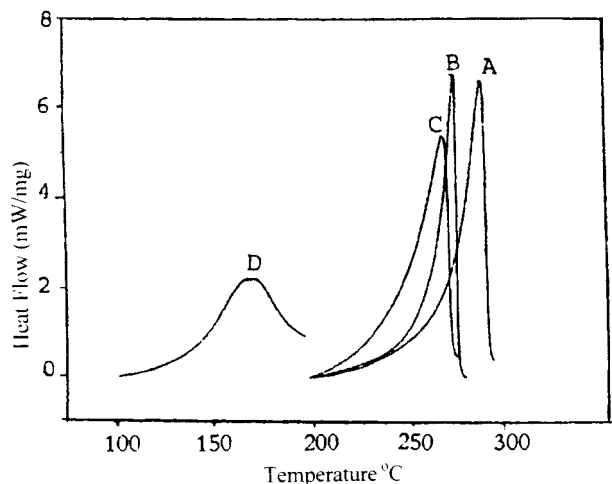


Figure 1 DSC scans of all the formulations at a 10°C/min heating rate.

with poly(vinyl alcohol) and layered with aluminum foil to act as a release agent. The cure schedule was followed at 130, 140, 150, 160, and 175°C for 1 h at each stage and 190°C for 4 h. In formulation **D** the cure schedule was 100°C for 1 h; 120, 130, 140, 150, 160, and 170°C for 1 h at each stage; and 190°C for 4 h.

RESULTS AND DISCUSSION

The present investigation was undertaken to evaluate the shelf life of epoxies with respect to substitution in the hardener system. The type of substituent determines the reactivity of the functional groups and hence dictates the curing reaction. In the context of studies involving electron withdrawing, chloro-substitution at the ortho and meta position with respect to the amine group was employed in determining the probable shelf life from thermal studies.

The dynamic DSC scans were carried out at heating rates of 2, 5, 10, and 15°C/min. Figure 1 shows the DSC scans of all formulations pertain-

ing to the 10°C/min heating rate. The initiation temperature (T_I), peak exothermic temperature (T_p), and completion temperature (T_f) of different formulations are tabulated in Table II.

The percentage of hardener used in these investigations was 20 phr in contrast to the normally used 30–40 phr hardener concentrations.⁵ This lower concentration of the hardener is reflected in the enhancement of the initiation temperature of all the formulations. The initiation temperature for the *o*-DCDDM system is the highest whereas that of formulation **D** with DDM is the lowest. This is a direct reference and a primary indication of the difference between shelf life of substituted and unsubstituted hardener systems. Thus, it may be observed that the *o*-DCDDM formulation has a longer shelf life than formulation **D**. However, the T_f was observed to be the highest and the total heat exotherm is more or less the same as that of the conventional DDS hardener. The kinetic parameters⁶ were calculated by employing the Ozawa and Kissinger equations:

$$E_a = -R\Delta \ln \phi / 1.052\Delta(1/T_p) \quad (1)$$

$$-\ln[\phi/T_p^2] = E_a/RT_p - \ln[AR/E_a] \quad (2)$$

where E_a is the activation energy, R is the gas constant, ϕ is the heating rate, $\ln A$ is the frequency factor, and T_p is the peak exotherm temperature of the corresponding ϕ . These were obtained from a variable peak exotherm of each formulation. The variable peak exotherm for formulation **D** is shown in Figure 2. The E_a from the Kissinger equation was calculated from the slope of the graph of $-\ln[\phi/T_p^2]$ versus $1/T_p$, which is equal to E_a/R . The graph between $-\ln[\phi/T_p^2]$ and $1/T_p$ for formulation **A** is shown in Figure 3. The E_a according to the ASTM E 698 method was calculated from the slope of the graph between $\ln \phi$ and $1/T_p$. A graph of $\ln \phi$ versus $1/T_p$ for formulation **A** is shown in Figure 4. The kinetic param-

Table II Cure Temperature and Heat of Cure for Epoxy Formulations at 10°C/min Heating Rate

Formulation	Resin System	T_I (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
A	TGDDM + <i>o</i> -DCDDM	213	287	294	689
B	TGDDM + <i>m</i> -DCDDM	175	273	279	631
C	TGDDM + DDS	187	267	275	710
D	TGDDM + DDM	120	166	203	334

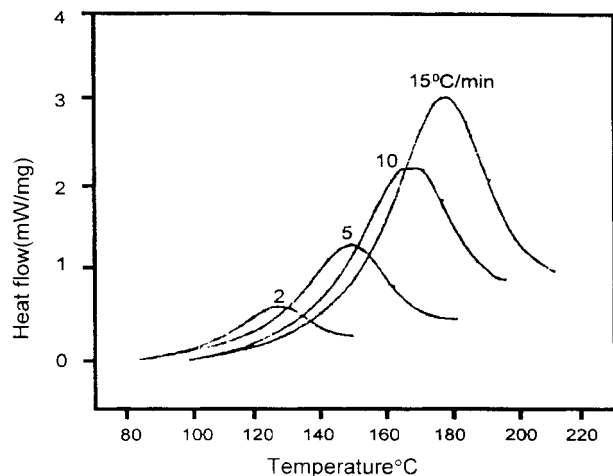


Figure 2 A graph of a common thermogram of formulation **D**.

eters of various formulations calculated from ASTM E-698 and the Ozawa and Kissinger equations are tabulated in Table III. In Table III it may be observed that the activation energy decreases from formulation **A** to **D**. Further, it may be noticed that the kinetic parameters obtained from different methods are comparable.

It is obvious from the results that the inclusion of chlorine as a substituent in the aromatic backbone has a pronounced effect on the cure kinetics of epoxies. Chlorine-substituted hardeners (formulations **A** and **B**) impart higher activation energies for corresponding epoxy formulations than the unsubstituted hardener system (formulation **D**). It may therefore be said that the reactivity of epoxy toward a hardener decreases with a decrease in the basicity of the hardener. A similar

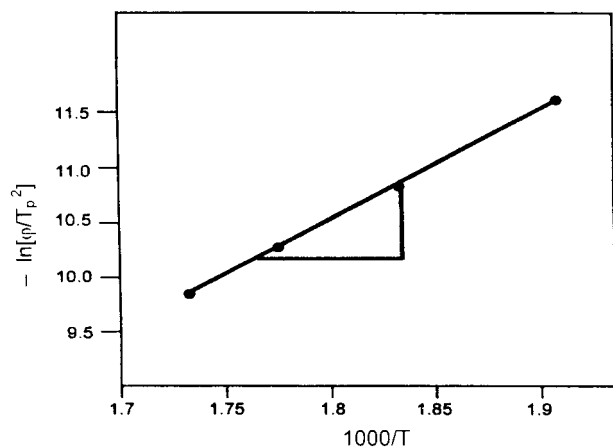


Figure 3 A graph of $-\ln[\phi/T_p^2]$ versus $1000/T$.

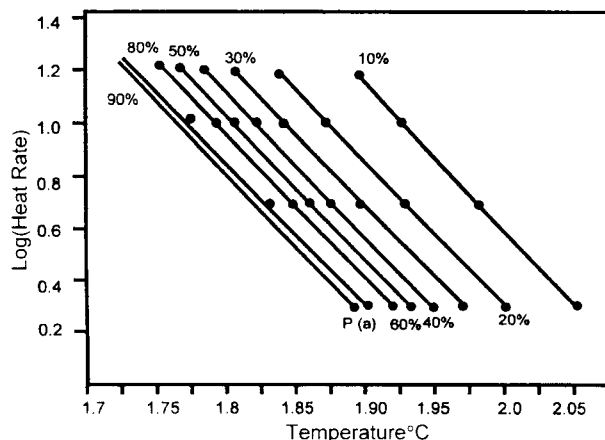


Figure 4 A graph of $\log(\text{heat rate})$ versus $1/T$ for formulation **A**.

analogy could be given in the reduction in the dissociation constants⁷ of aniline (4.2×10^{-10}), *m*-chloroaniline (0.3×10^{-10}), and *o*-chloroaniline (0.05×10^{-10}) with respect to the chloro-substitution, wherein the introduction of chlorine in the aromatic ring decreases the basicity of the amino group more in the ortho than meta position. On this basis one can assign the highest basicity among the three hardeners to unsubstituted DDM and the lowest to *o*-DCDDM. Hence, *o*-DCDDM is the least reactive of the three and this explains the highest activation energy of the corresponding formulation **A**.

The difference in the activation energies of chlorine-substituted hardener formulations (**A** and **B**) and unsubstituted hardener formulation **D** cannot be attributed to the electronegativity of the chlorine substituent alone. However, there could be a contribution from steric hindrance to the lower reactivity of the hardener. As the reaction proceeds, especially in the vitrification region, this steric hindrance factor will have a pronounced effect on the rate of the reaction where segmental mobility becomes the determining factor for the rate of the reaction. Hence, the higher activation energy of substituted hardener formulations is also due to the steric hindrance caused by the chlorine substituent, especially in the ortho position. This is supported by the fact that even the presence of electron releasing groups like the $-\text{CH}_3$ substituent at the ortho position of DDM is reported to increase the activation energy in the latter stages of the reaction.⁸ This indicates that the steric factor does have a greater impact on the reaction rate, especially in the later stages of the reaction, irrespective of the inductive effect of the functional group.

Table III Kinetic Parameters Obtained by Various Methods

Formulation	E_a (kJ/mol)			Frequency Factor (ln A min ⁻¹)		60-min Half-Life Temp.
	a	b	d	a	b	
A	88	98	98	8.102	10.4	205.3
B	87	96	92	7.56	9.65	193.5
C	82	93	88	7.32	9.54	188.9
D	51	51	51	5.52	9.07	83.9

a, ASTM E 698; b, Kissinger method; d, Ozawa method.

From the values given in Table II it may be noted that, even though the reaction in *m*-DC-DDM (formulation **B**) starts earlier (175°C) compared to the DDS formulation (187°C), it ends a little later (273°C) than the DDS system (267°C). This shows that *m*-DCDDM is more reactive than DDS and its reaction rate becomes slower as the reaction proceeds, which means that the bulky chlorine atom hinders the mobility due to the steric effect in the hardener.

Evaluation of Shelf Life

The shelf life of various TGDDM formulations was calculated by following residual cure exotherms using dynamic DSC. In this method residual cure exotherms of various formulations were measured at equal intervals of time. The fractional conversions of epoxy groups (α) at different time intervals were calculated from residual cure exotherms using the following equation:

$$\alpha = \frac{\Delta H_{\text{RXN}} - \Delta h_t}{\Delta H_{\text{RXN}}} \quad (3)$$

where ΔH_{RXN} is the total heat of the reaction, Δh_t is the heat of the reaction at time t , and $\alpha = 0.3$ is taken as the limit for the shelf life. The graph of $(1 - \alpha)$ versus the time is shown in Figure 5. From the graph it may be observed that DDM formulation **D** was 65% cured within 10 days and afterward the change in the α is negligible; formulation **A** was found to undergo curing after a minimum of 40 days and thereafter a negligible change was observed in the α .

This is an indication of higher shelf life for formulation **A** compared to formulation **D**. In formulations **B** and **C** the percentage of cure is almost the same (33 and 35%, respectively) even

after 40 days, which is reflected in their 60-min half-life temperature as shown in Table III.

Mechanical Properties

For a complete understanding of the behavior of the resin formulations and their mechanical properties an evaluation was made with cast specimens of all four systems under consideration. Properties such as the tensile, flexural, and impact strengths and the glass-transition temperature (T_g) of formulations **A–D** were determined and are summarized in Table IV. The table shows that there is no significant change in the tensile modulus and flexural strength of chloro-substituted and unsubstituted hardener formulations (**A**, **B**, and **D**). However, the tensile strength of formulation **A** is lower than **D** while that of formulation **B** is higher than **D**. This may be attributed to the partial curing of the resin in the

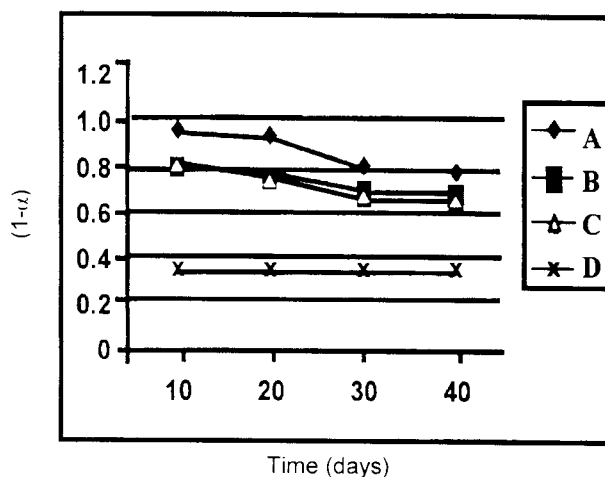


Figure 5 A graph of $(1 - \alpha)$ versus time for all the formulations.

Table IV Mechanical Properties and Glass-Transition Temperature of Various Formulations with 20 phr Hardener and Postcured at 190°C for 4 h

Property	Formulation			
	A	B	C	D
Tensile strength (MPa)	37 (2.42)	56 (2.586)	54 (0.99)	46 (0.08)
Elongation (%)	3.9 (0.232)	4.0 (0.238)	3.0 (0.11)	6.25 (0.12)
Tensile modulus (GPa)	1.9 (0.045)	2.2 (0.355)	3.0 (0.05)	2.0 (0.05)
Flexural strength (MPa)	99 (1.731)	90 (1.090)	80 (2.17)	100 (3.2)
Izod impact strength (J/m)	11.9 (0.23)	10.7 (0.169)	9.0 (0.1)	14.0 (0.13)
T_g (by DMA, °C)	190 (1.0)	200 (2.8)	210 (2.0)	192 (1.5)

The values shown in parentheses are standard deviations.

former case under the same curing conditions, as evidenced by the lower tensile modulus.

The values of the impact strength (Table IV) reveal that formulation **D** exhibits the highest impact strength. A comparison of the impact strengths of formulations **A**, **B**, and **D** reveals that the substitution of chlorine into the aromatic ring of DDM decreases the impact strength. This may be attributed to the degree of flexibility exhibited by each of the hardener molecules. In *o*-DCDDM (**A**) and *m*-DCDDM (**B**) the flexibility is restricted because of the substitution of the bulky chlorine group. This is further supported by the percentage of elongation exhibited by these formulations.

The DMA curves for formulations **A–D** are shown in Figure 6. The temperature corresponding to the peak of the loss modulus curve is taken as the T_g . It was observed that the T_g of formulation **A** is comparable to that of formulation **D**, while the T_g of formulation **B** is higher than that

of formulation **D**. The increment in the T_g with *m*-DCDDM as the hardener can be attributed to the steric hindrance caused by the bulky chlorine atom. A similar improvement in the heat distortion temperature was observed in the DGEBA in comparison with tetrabromo-DGEBA used by Shrimp and Wentworth.⁹ They attributed this rise in the heat distortion temperature due to the bulkiness of the bromine atom. The lower T_g of *o*-DCDDM formulation **A** may be due to the undercuring of the formulation resulting from the lower reactivity of the amine. The T_g values are lower in formulations **A**, **B**, and **D** compared to DDS formulation **C**.

CONCLUSIONS

The effect of chlorine as a substituent in the aromatic backbone of the curing agents at different positions as revealed by cure kinetics and mechanical properties were studied in comparison with the unsubstituted hardener systems DDM and DDS. The study reveals the following points:

1. Formulations with chlorine substitution increased the shelf life of the epoxy resin compared to the unsubstituted resin formulation and were higher than the most widely used DDS hardener system. The formulation with chloro-substitution at different positions had a narrow difference in their activation energies, and no significant variation in the overall mechanical properties.
2. The T_g was found to be slightly higher for the *m*-DCDDM formulation; although there is less stoichiometric content of

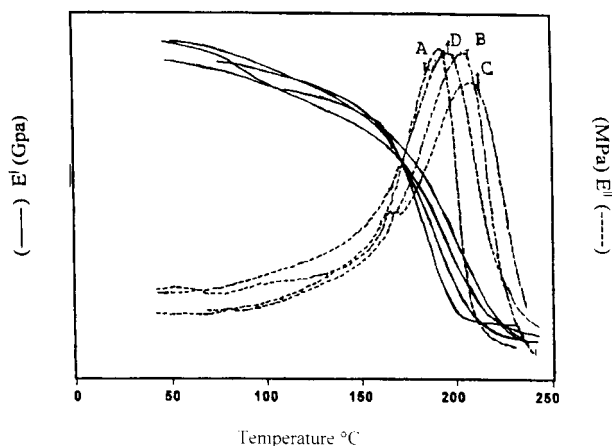


Figure 6 DMA curves for all the formulations.

amine, the T_g values of the *o*-DCDDM and DDM formulations were found to be almost the same.

3. The impact strength decreased for the formulations with chloro-substituted hardeners, irrespective of the position of substitution, but it is higher when compared to the conventional DDS system.
4. The tensile modulus and flexural strength of the formulations were found to have no major change, although they had different stoichiometric ratios of amine concentration. However, a slight variation in the tensile strengths was observed in the substituted systems.

The authors thank the Office of Naval Research, Naval Research Laboratory (Washington, DC), for the sanction of our research. We also thank Drs. C. Biswas and A. V. Rajanna (ARDC, HAL, Bangalore) for their help in carrying out the DSC studies.

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