

Cure Kinetics of Multifunctional Epoxies with 2,2'-Dichloro-4,4'-Diaminodiphenylmethane as Hardener

K. S. JAGADEESH,¹ J. GURURAJA RAO,¹ K. SHASHIKIRAN,¹ S. SUVARNA,¹ SARVOTTAM Y. AMBEKAR,¹ MURALI SALETORE,² C. BISWAS,² A. V. RAJANNA²

¹ Central Institute of Plastics Engineering & Technology, Mysore 570 016, India

² Hindustan Aeronautics Limited, Bangalore 560 037, India

Received 6 May 1999; accepted 22 September 1999

ABSTRACT: The curing behavior of the epoxy resin *N,N,N',N'*-tetraglycidyl-diaminodiphenyl methane (TGDDM) with triglycidyl *p*-aminophenol as a reactive diluent was investigated using 2,2'-dichloro-4,4'-diaminodiphenylmethane (DCDDM) as the curing agent. The effect of the curing agent on the kinetics of curing, shelf-life, and thermal stability in comparison with a TGDDM-diaminodiphenylsulfone (DDS) system was studied. The results showed a lesser activation energy at the lower level of conversion with a broader cure exotherm for the epoxy-DCDDM system in comparison with the epoxy-DDS system, although the overall activation energy for the two systems was comparable. TGA studies showed more stability in the epoxy-DCDDM system than in the epoxy-DDS system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2097–2103, 2000

Key words: multifunctional epoxy resins; curing kinetics

INTRODUCTION

In view of the significant weight savings in many applications including aeronautics, high-performance composites have gained increasing importance in recent years. In many cases, these composites are based on *N,N,N',N'*-tetraglycidyl-diaminodiphenyl methane (TGDDM). This resin matrix offers very good mechanical properties, even up to temperatures above 200°C,^{1–3} after curing with suitable curing agents. Curing agents such as halophenyl methanes and halogenated diphenyls are reported to increase the fire retardant properties of the composites based on epoxy resins.⁴ A survey of the literature also shows that very little work has been carried out on the use of halogenated 4,4'-diaminodiphenylmethanes (DDM) as curing agents. The only reference we found is

described in a patent⁵ in which the *m*-chloroaniline–HCHO complex is used as a curing agent. With this in view, studies on 2,2'-dichloro-DDM (DCDDM) as a hardener were undertaken. Earlier we reported the kinetic parameters and the mechanism of curing of a TGDDM-diaminodiphenylsulfone (DDS) system⁶ using triglycidyl *p*-aminophenol (TGPAP) as a reactive diluent; it reduces the viscosity of the resin for ease of processing with minimum effect on the ultimate properties. In continuation of our work the present article describes the modified synthesis of DCDDM and its effect as a curing agent on the kinetics of curing, the shelf-life of the resin, and the thermal stability of the composite in comparison with the TGDDM-DDS system.

EXPERIMENTAL

Materials

The DDS (Fluka), *p*-aminophenol (Fluka), epichlorohydrin (Fluka), and DDM (Fluka) were

Correspondence to: K. S. Jagadeesh (cipstmys@blr.vsnl.net.in).

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

Journal of Applied Polymer Science, Vol. 77, 2097–2103 (2000)
© 2000 John Wiley & Sons, Inc.

Table I Formulations of Epoxy with wt 30 % Curing Agent Systems

Resin System	Formulation	Composition Weight (Resin %)
TGDDM + DCDDM	IA	100
TGDDM + DDS	IB	100
TGPAP + DCDDM	IIA	100
TGPAP + DDS	IIB	100
TGDDM + TGPAP + DCDDM	IIIA	90 : 10
TGDDM + TGPAP + DDS	IIIB	90 : 10
TGDDM + TGPAP + DCDDM	IVA	80 : 20
TGDDM + TGPAP + DDS	IVB	80 : 20
TGDDM + TGPAP + DCDDM	VA	70 : 30
TGDDM + TGPAP + DDS	VB	70 : 30

used as received. Ethanol, methyl ethyl ketone, and acetone were used after distillation.

The TGDDM was synthesized according to the procedure described in our previous article.⁶ The product used had an epoxy equivalent weight of 120 g/mol, a hydrolysable chlorine content of 1.4%, and a viscosity of 10,000 cps at 25°C. The TGPAP resin used had an epoxy equivalent weight of 105 g/mol, a hydrolysable chlorine content of 1.1%, and a viscosity of 8000 cps.

The DCDDM was synthesized by modifying the literature method.⁷ Its reaction time was reduced from 65 to 6 h and the reaction temperature was maintained at 70°C instead of the reflux temperature. Introduction of column chromatography improved the yield from 28 to 45%.

Preparation of DCDDM

m-Chloroaniline (64 g) was added dropwise to a solution of distilled water (100 mL) and concentrated HCl (47 mL) placed in a round bottom flask. The contents were stirred and the reaction mixture was cooled to 15°C. Formaldehyde (18 g, 40% w/v) was then added dropwise to the reaction mixture. After the addition was complete, the reaction mixture was heated for 6 h at 70°C. The mixture was then cooled, basified with sodium bicarbonate (10% aqueous solution), and subjected to steam distillation. The distillate was extracted with chloroform and dried over anhydrous sodium sulfate. After distilling off the chloroform, the brownish oily substance thus obtained was subjected to column chromatography using a silica gel column and chloroform as the eluent. The desired product was obtained as the fourth fraction as shown by TLC. This fraction was distilled off and DCDDM was recrystallized from a hexane-chloroform mixture into a white

crystalline product. Yield: 13 g (45%); mp 102–103°C (lit.⁷ 102.5–103.5°C); IR: γ NH₂, 3400 cm⁻¹ and γ C=C, 1610 cm⁻¹; NMR (CDCl₃, ppm): δ 6.8 (2H, s, 3, 3'H), 6.65 (2H, d, 5, 5'H), 6.4 (2H, q, 6, 6'H), 3.9 (2H, s, —CH₂), and 3.55 (4H, s, —NH₂).

Methods

The curing studies were carried out on TA-DuPont 2100 DSC. The thermal stability of the cured specimens was determined by using a TA-DuPont 2100 TGA module. The formulations studied under DSC and TGA are given in Table I.

Sample Preparation for DSC Studies

To an accurately weighed 2 g of resin or resin formulation (TGDDM with TGPAP as diluent) was added 0.6 g of the hardener, and it was heated to 80°C for uniform dispersion and stored at room temperature. A small quantity of the sample (8–12 mg) was taken for DSC studies in an aluminum cell. An identical empty cell was taken as reference.

DSC Measurements

A small quantity of the sample was weighed into the aluminum cell. The dynamic scans were taken in a nitrogen atmosphere at heating rates of 2, 5, 10, and 15°C/min in the range from ambient to 300°C. Ozawa and Kissinger equations were adopted to evaluate the curing kinetic parameters.

Sample Preparation for TGA Studies

Two grams of resin or the resin formulation (resin–diluent proportion) were accurately weighed and 0.6 g of the hardener was added, and the

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

Formulation	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
IA	120	252	270	593.9
IB	136	251	271	612.0
IIA	114	232	242	554.5
IIB	120	226	246	578.0
IIIA	116	239	250	556.0
IIIB	132	247	254	640.0
IVA	114	240	255	601.0
IVB	127	240	258	567.0
VA	111	238	247	568.0
VB	125	239	253	581.0

sample was cured at 180°C for 2 h and postcured at 200°C for 3 h.

TGA Measurement

A small quantity (5–8 mg) of the cured epoxy sample was taken in the TGA pan, and the weight loss was observed in the dynamic scan with a heating rate of 10°C/min. The thermal stability of the neat resin cast was then recorded from the thermogram.

RESULTS AND DISCUSSION

The curing behavior of TGDDM based epoxy formulations with DCDDM as the curing agent in comparison with that of DDS was studied by DSC. The dynamic DSC scans of epoxy-DCDDM and epoxy-DDS systems were taken at different heating rates with 30% by weight of the curing agent. The dynamic curing exotherms of the resin formulations were recorded and the initiation temperature, T_i , peak exotherm temperature, T_p , and temperature of completion, T_f , of the thermograms along with the heat of cure are given in Table II. Typical dynamic DSC scans with a 10°C/min heating rate obtained for epoxy-DCDDM and epoxy-DDS systems are shown in Figures 1 and 2.

It may be observed from the figures that the epoxy-DCDDM system gives an inflection in the curing exotherm in contrast to the epoxy-DDS cure curve. The inflection peak of the epoxy-DCDDM system (120–200°C) may be due to the primary amine-epoxide reaction leading to a linear polymer and second and the main peak exotherm is due to the crosslinking reaction involving the secondary amine-epoxide (200–260°C). Similar multiple peak exotherms are reported by Chowdhary et al.⁸ in the TGDDS-DDS system.

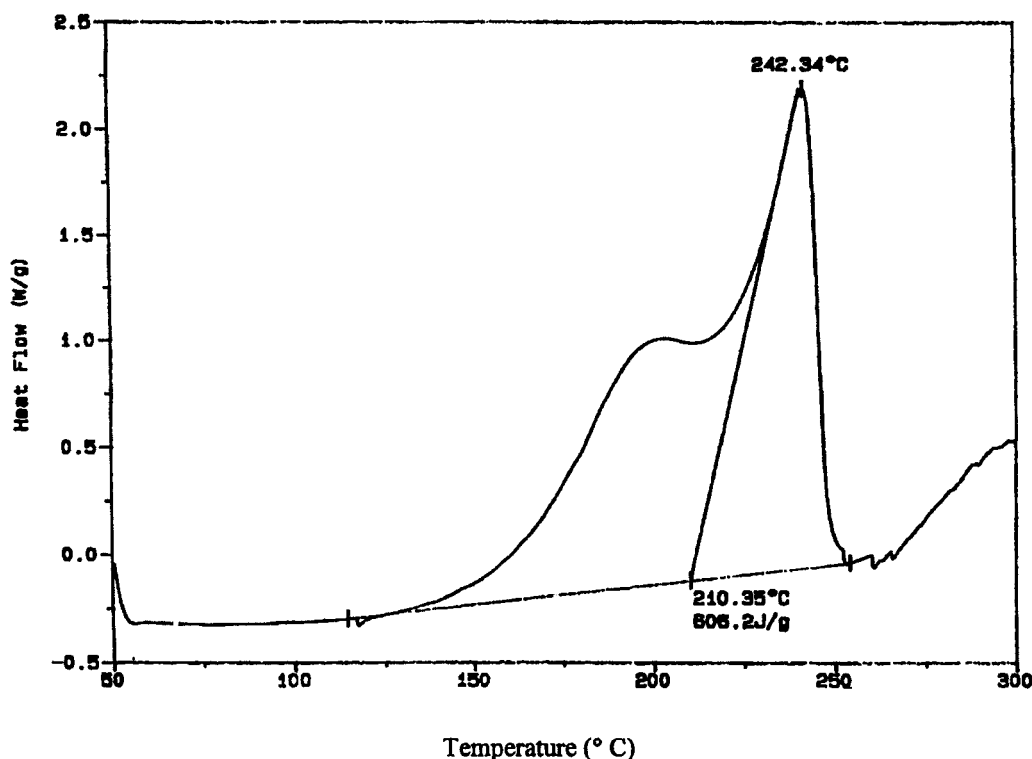


Figure 1 A typical DSC scan of the epoxy-DCDDM system for formulation IVA.

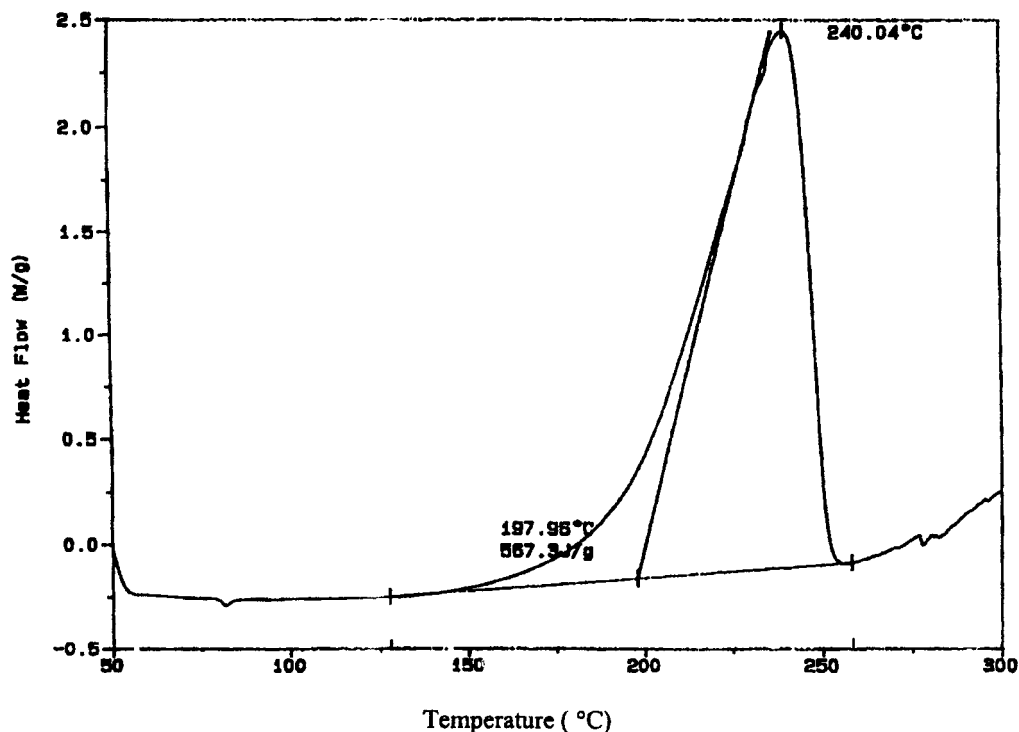


Figure 2 A typical DSC scan of the epoxy-DDS system for formulation IVB.

However, Siddaramaiah et al.⁹ reported only one exotherm for the TGDDM-DDM system in the range of 150–250°C, indicating that the activation energy for linear polymerization and crosslinking reactions are equal. Considering the comparable basicity of the DDM and DCDDM molecules, there should have been only one peak in the TGDDM-DCDDM system. However, the appearance of the second exotherm at the higher temperature can be attributed to steric hindrance during the crosslinking reaction that is due to the bulky chlorine atom in DCDDM.

The observation of a single exotherm peak in the epoxy-DDS system, in contrast to the two exotherms of the epoxy-DCDDM system, reveals that the linear and crosslinking reactions take place at almost the same temperature

range. That means the first step of the reaction between DDS and the epoxy resin is hindered in comparison with the reaction between DCDDM and the epoxy. This is quite obvious because of the reduced basicity of the primary amine group in DDS that is due to an electron-withdrawing resonance effect of the sulfonyl group. The first step of the reaction in the primary amines without any electron-withdrawing group in the molecule of the curing agent takes place in a lower temperature range as observed in the TGDDM-DDM system.⁹

The kinetic parameters were evaluated by the variable peak exotherm method. Table III shows the kinetic parameters obtained from the Kissinger equation, eq. (1), at various heating rates for the representative epoxy formulation IVA:

Table III Kinetic Parameters of TGDDM : TGPAP + DCDDM (80 : 20 + 30) Obtained by Kissinger Equation

Heating Rate (°C/min)	$1/T_p$	$-\ln(\phi/T_p^2)$	E_a (kJ/mol)	$\ln A$ (min^{-1})
2	0.002087	-11.6502	84	14
5	0.002004	-10.8157	84	13.1
10	0.001941	-10.185	84	12.5
15	0.001904	-9.8187	84	12.3

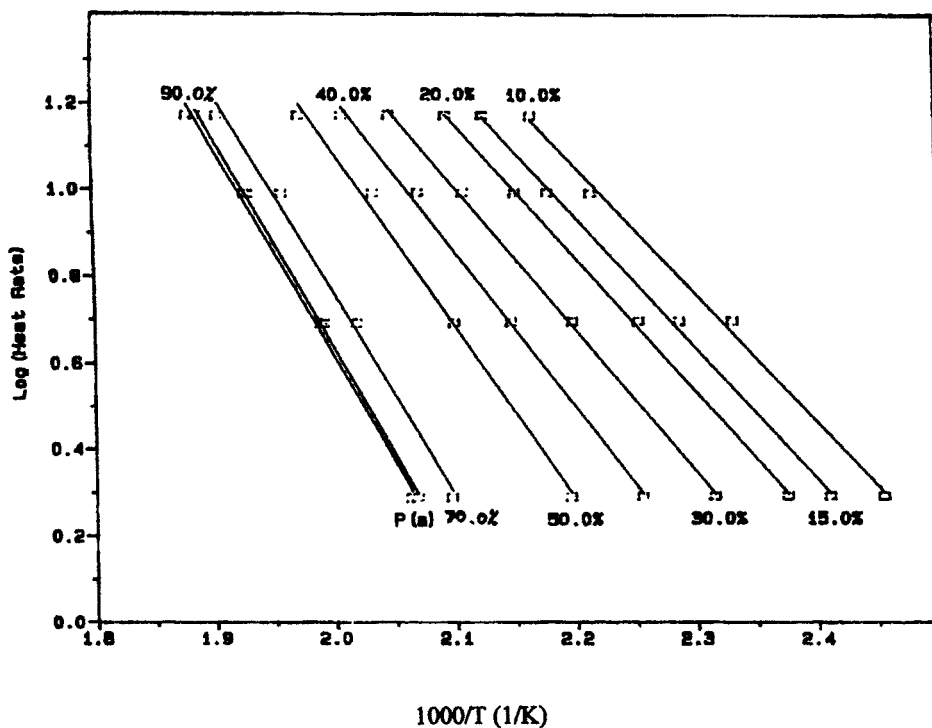


Figure 3 A plot of $1/T$ vs. $\log(\text{heat rate})$ showing the kinetic linear relationship for formulation **IVA**.

$$-\ln(\phi/T_p^2) = E_a/RT_p - \ln(AR/E_a) \quad (1)$$

$$E_a = -R\Delta \ln \phi / 1.052\Delta(1/T_p) \quad (2)$$

where ϕ is the heating rate, T_p is the peak exothermic temperature, R is the gas constant, and A is the frequency factor.

The activation energy, E_a , for various resin formulations was also determined by the Ozawa equation, eq. (2).

The graph of $\ln \phi$ versus $1/T$ obtained by the ASTM E-698 method, which assumes first-order kinetics, is shown in Figure 3 for formulation **IVA** at different conversion levels. The results obtained are given in Table IV along with the activation energy for a 30% conversion according to

Table IV Kinetic Parameters Obtained by Kissinger and Ozawa Equations for Epoxy Formulations with 30% Hardener

Formulation	E_a (kJ/mol)		Frequency Factor	E_a at 30% Conversion ASTM E 698
	Ozawa	Kissinger		
IA	96	98	13.1	53.1
IB	86	78	12.9	69.5
IIA	80	78	12.8	42.5
IIB	73	73	12.74	55
IIIA	94	91	13.05	52.4
IIIB	80	82	12.87	60.9
IVA	86	84	12.97	51.2
IVB	80	78	12.85	60
VA	81	86	12.9	50.6
VB	79	77	12.84	59

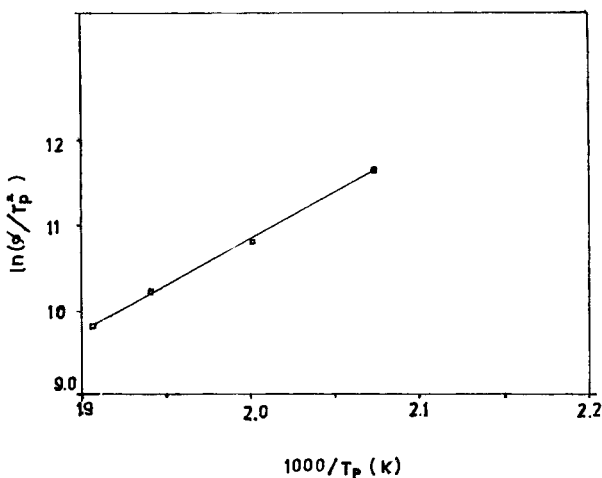


Figure 4 A graph of $\log \phi$ vs. $(1/T)$ for formulation **IVA**.

the ASTM E-698 method. The plot of $1/T$ versus the $\log(\text{heat rate})$ shows a linear relationship as shown in Figure 4 for formulation **IVA**, which was obtained by adopting the Kissinger equation.

The activation energy at lower conversion levels is less for the formulation with DCDDM as compared to DDS systems. At the T_p the formulation with DCDDM possesses a higher activation energy in comparison with the same resin formulation with DDS as the curing agent. Further, we found that there was no appreciable change in the frequency factor of various resin formulations.

It is apparent from the comparison of the DSC thermograms shown in Figures 1 and 2 that the cure initiation temperature of the resin formulation with DDS as the hardener is higher (150°C) than that of the resin formulation with DCDDM as the hardener (125°C), indicating a lower shelf-life for the epoxy-DCDDM system. Further, it is supported by calculating the fractional area under the exothermic curve required for 30% conversion in each case. We found that the formulation with DDS as the hardener requires a higher temperature by up to nearly 30°C .

TGA Results

The typical TGA curves of the two different resin formulations are shown in the Figure 5. The weight loss follows the same path except for the initial temperature of degradation. Table V shows the temperature at 5% weight loss of the cured epoxy formulations and the residual weight at 600°C .

Table V shows that a 5% weight loss occurs at 300°C for the DCDDM system whereas it is 270°C for the DDS cured system. A trend of increased thermal stability is observed in all formulations wherein the DCDDM cured epoxies are stable by over $30\text{--}35^\circ\text{C}$ in contrast to DDS cured epoxies.

CONCLUSIONS

The results of the thermal stability studies reveal that the DCDDM-epoxy system outperforms the

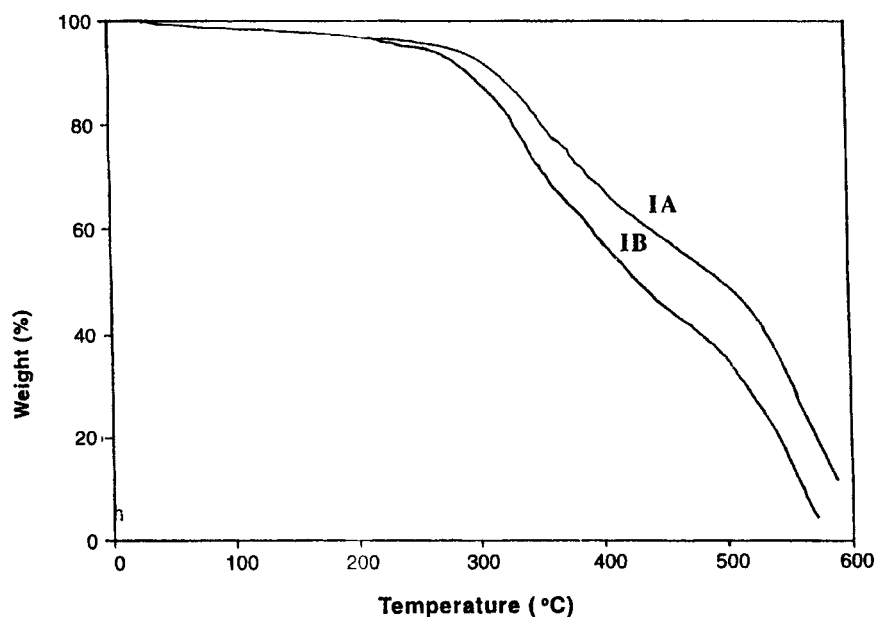


Figure 5 The typical TGA curves obtained for formulations **IA** and **IB**.

Table V Temperature Data at 5% Weight Loss of Cured Epoxy Formulations

Formulation	Temperature at 5% Weight Loss (°C)	Residual Weight at 600°C (%)
IA	300	12.3
IB	270	4.66
IIA	261	11.8
IIB	250	2
IIIA	290	13
IIIB	265	8
IVA	284	10
IVB	260	7
VA	269	13
VB	258	7

DDS system because the thermal stability is increased by over 30–35°C. The overall activation energy of the epoxy-DCDDM system is marginally higher than the epoxy DDS cured system.

The apparent activation energy is less at lower conversion levels and possesses a lower initiation temperature in the DCDDM-epoxy system, indicating a lower shelf-life; but the completion of cure still requires heating to temperatures of 250–270°C. Thermograms indicate a wider cure

exotherm for the DCDDM-epoxy cured system (125–260°C) than the DDS-epoxy cured system (150–260°C).

The discussions the authors had with Dr. Siddaramaiah are hereby acknowledged.

REFERENCES

1. Thosaby, M. R.; Dobinson, B.; Bull, C. H. *Br Polym J* 1986, 18, 286.
2. Dobas, I.; Podzimek, S.; Pacheidt, J.; Patev, N.; Becvar, L. *Polim (Warsz)* 1989, 34, 24.
3. Dobas, I.; Lunak, S.; Zelenka, J.; Horalek, J.; Spacek, N.; de Petris, S. *J Appl Polym Sci* 1992, 45, 923.
4. Mika, T. F.; Bauer, R. S. In *Epoxy Resins*; May, C. A., Ed.; Marcel Dekker: New York, 1988; p 476.
5. (a) Smith, C. M. (to General Aniline and Film). U.S. Pat. 3,071,559; (b) Smith, C. M. In *Epoxy Resins*; May, C. A., Ed.; Marcel Dekker: New York, 1988.
6. Jagadeesh, K. S.; Siddaramaiah; Kalpagam, V. *J Appl Polym Sci* 1990, 40, 1281.
7. Gorvin, J. H. *J Chem Soc* 1955, 83.
8. Choudhary, V.; Verma, I. K.; *J Appl Polym Sci* 1993, 49, 1752.
9. Siddaramaiah; Jagadeesh, K. S.; Prabhakara, G. *Ind J Eng Mater Sci* 1996, 3, 114.