A Study on the Effect of New Cyanate and Phenoxy Polymer on TGDDM/DDS/GMP Formulations

M. Suguna Lakshmi, M. Srividhya, B. S. R. Reddy

Industrial Chemistry Laboratory, Central Leather Research Institute, Chennai 600 020, India

Received 17 May 2002; accepted 28 August 2002

ABSTRACT: An attempt was made on the modification of the tetraglycidyl-4,4′-diaminodiphenyl methane/diaminodiphenyl sulfone (TGDDM/DDS) system to improve properties for several industrial applications. Epoxy resins [TGDDM and 1-glycidyloxy-4-methoxy phenol (GMP)] were synthesized in the laboratory. Also, a new cyanate ester and phenoxy polymer were synthesized and characterized by FTIR, ^{1}H-/^{13}C-NMR, and thermal studies. GMP was added as a diluent and a new cyanate ester (DCDPT) was introduced to reduce the tight crosslinking density. Further, a new phenoxy polymer was added to improve the toughness property. A variety of neat resin casts using different compositions of the blends were made and their physical, chemical, thermal, and mechanical properties were evaluated to study the effect of GMP as a diluent, cyanate ester as a comonomer, and phenoxy polymer as a toughener. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2963–2973, 2003

Key words: crosslinking; resins; toughness

INTRODUCTION

Epoxy resins have increasing demand in a variety of applications such as matrix resins, carbon fiber reinforced composite materials for aerospace applications, reinforced plastic materials for molding compounds, insulating materials for printed circuit boards, various electric and electronic components, and also as structural adhesives and coating compounds.

Epoxy resins exhibit low shrinkage and no volatile formation upon curing. Once epoxy resins are cured, they display high heat, corrosion, and chemical resistivity along with excellent mechanical properties. Generally, epoxy resins with mono-, di-, tri-, and tetrafunctionalities are used for curing. Because the epoxy group is reactive to many substances (amines, amides, imides, acids, anhydrides, and cyanate esters), crosslinked epoxy resins are obtained through rearrangement polymerization reaction method.

Tetraglycidyl-4,4′-diaminodiphenyl methane (TGDDM) cured by diaminodiphenyl sulfone (DDS) is widely used as reinforced plastic material for making composite materials. The TGDDM/DDS system is known for high thermal stability and good mechanical strength. However, they suffer from high brittleness and low moisture resistance. These two drawbacks severely affect the mechanical properties and lead to poor utility of the materials. To overcome these drawbacks, modification of the TGDDM/DDS system became inevitable[1–3] for further detailed research.

In an attempt to modify the TGDDM/DDS system to reduce brittleness, which is one of the drawbacks, 1-glycidyloxy-4-methoxy phenol (GMP) was added as a diluent and its mechanical properties were evaluated. Further, a new cyanate ester with rigid aromatic backbone was introduced into the TGDDM/DDS system to reduce the tight crosslinking density of the polymer. Curing of epoxy–cyanate reaction is faster than that of the neat epoxy system. The addition of cyanate ester in epoxy improves the thermal stability and reduces the density of the cure network of epoxy polymer because of the oxazolidinone and triazine ring formations. Highly crosslinked epoxy resins are essential to obtain high heat-resistant composite materials. Because tight crosslinking results in brittle thermosetting polymers, several approaches were made to decrease the brittleness or to increase the toughness of the materials for various applications. Accordingly, a number of studies were reported concerning the application of toughening agents such as liquid rubbers, thermoplastics, and silicones.

Yee and Pearson[4] studied the inclusion of rubber as a second phase to epoxy resin, where the rubber particles act as stress concentrators enhancing the shear localization. Toluene diisocyanate acts as a coupling agent between epoxy and rubber, which increased the mechanical properties.[5] Although toughness had been improved, the glass transition temperature and the resin modulus properties were greatly affected.[6–8]

A large number of studies were undertaken on the inclusion of thermoplasts, such as polysulphones,[9]

Correspondence to: B. Reddy (induchem2000@yahoo.com).

Journal of Applied Polymer Science, Vol. 88, 2963–2973 (2003)
© 2003 Wiley Periodicals, Inc.

polyethersulphones,[10] and polyetherimide,[11] to epoxy networks. These studies show good improvement in thermal and mechanical properties.[12] Nevertheless, these polymers show poor solubility in organic solvents leading to difficulties in processing. To overcome this difficulty, we have taken up the present work to design and synthesize a new phenoxy polymer.

Phenoxy resins are tough and ductile thermoplastic materials that exhibit high impact and cohesive strength.[13] They are efficient flexibilizers[14,15] for a variety of polymers, including epoxy resins. The repeating unit of their linkages and pendant hydroxyl group facilitates the wetting and bonding to polar substrates.[16] The phenoxy polymer introduced possesses low melting point and shares structural similarity with bisphenol-A epoxy resin. Because both constituents bear similar structural backbone, complete miscibilization without any solvent and reduced phase separation is expected in the cured network structure.

Therefore, the purpose of this work was to explore the effect of a new kind of cyanate ester as a comonomer and phenoxy polymer as a toughener, along with GMP epoxy as a diluent in the TGDDM/DDS system. Neat castings were prepared from the blended formulations of cyanate ester and phenoxy polymer with TGDDM/DDS/GMP. The physical, chemical, and mechanical properties were evaluated.

EXPERIMENTAL

Materials

4-Methoxy phenol, bisphenol-A, epichlorohydrin, dimethylaniline, cyanogen bromide, and imidazole were obtained from SD Fine Chemicals (Mumbai, India). Terephthaloyl chloride, triethylamine, and 4,4′-diaminodiphenyl methane were purchased from Acros Organics (Belgium).

Epichlorohydrin was purified by vacuum distillation at 70°C. Bisphenol-A was recrystallized from acetone.

Epoxy equivalent weight (EEW) measurements

EEW was determined by employing the pyridinium hydrochloride method.[17]

FTIR and ^{1}H-/^{13}C-NMR spectroscopy

A Perkin–Elmer FTIR spectrophotometer Model 20 DXB was used to record the IR spectrum (400–4000 cm^{-1}) of monomers and cured samples. Analyses were done by using solid KBr pellets. ^{1}H-/^{13}C-NMR studies of the compounds were done on a Bruker 310 MHz spectrophotometer at room temperature by using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard.

Thermal analysis

Thermogravimetric analyses (TGA) of the epoxy formulations were investigated on a Mettler TA4000 at a heating rate of 10°C/min in nitrogen atmosphere.

Differential scanning calorimetry (DSC)

The DSC data were obtained by using 8- to 10-mg samples in nitrogen atmosphere at a heating rate of 20°C/min on a Perkin–Elmer analyzer model DSC 7.

Gel permeation chromatography (GPC)

GPC analysis was performed by using a phenomenex gel column (Shimadzu) with a dimension of 300 × 7.8 mm. Tetrahydrofuran was used as mobile phase with a flow rate of 0.3 mL/min at ambient temperature.

Scanning electron microscope (SEM) analysis

SEM analysis was done for the samples by using Stereo Scan Model 440 (Oxford) at a magnification of 4000×.

Mechanical properties

The mechanical properties were investigated by using a universal testing machine (Model HTE-S-Series-H50K-S, Hounsfield Test Equipment Ltd., UK).

Tensile properties

Specimens having 25 mm width, 200 mm length, and 3 mm thickness were used. The crosshead speed was 2 mm/min. The span length of the specimens was 115 mm.

Tensile strength and tensile modulus studies were evaluated as per the procedure given in ASTM D 3039.

Flexural properties

The flexural strength and flexural modulus studies were done as per ASTM D 790 by using specimens having 10 mm width, 90 mm length, and 3 mm thickness. Crosshead speed was 2 mm/min.

Shore D hardness

The hardness test was performed by using a Shore D hardness tester according to the procedure given in ASTM D 785.

TABLE I
Compositions for the Preparation of Systems (I–V) (wt %)

Resin system	TGDDM	GMP	DCDPT	DDS	Phenoxy polymer
I	—	—	100	—	—
II	—	—	—	—	100
III	60	4.76	—	32.5	—
IV	60	4.76	10	32.5	—
V	60	4.76	10	32.5	10.7

TGDDM and DDS were taken at the equivalent ratio of 4 : 2 (epoxy : amine).

Impact strength

The unnotched Izod impact strength was measured according to the ASTM D 256-88 method. Specimens of 65 mm length, 10 mm width, and 3 mm thickness were used for testing.

Water and chemical resistance

Percentage of water absorption at room temperature (RT) and elevated temperature (85°C) for 24 h was evaluated. The chemical resistance properties of the cured specimens in acetone, 10% NaOH, 10%HCl were also evaluated. Samples with a size of 25 mm length, 25 mm width, and 3 mm thickness were immersed for 24 h in the solvent, removed, and wiped with tissue paper, and their weights were checked until they reached a constant weight.

Fabrication of modified neat resin castings

Employing the compositions given in Table I, formulations of TGDDM with GMP, DDS, cyanate ester, and phenoxy polymer were made. The blends were thoroughly mixed and melted at 120°C in an oil bath to get a homogeneous liquid. They were transferred to a preheated open mold at 120°C coated with silicone-based sealant to facilitate release of the cured samples. It was then heated to 130°C and deaerated under vacuum for 0.5 h to drive the air bubbles from the castings.[18] All the castings were heated to cure at 130°C for 4 h. The cured laminates were then removed from the mold and curing was continued at 150°C for 2 h and further cured at 180°C for 2 h. The cured samples were cut to suitable dimensions required for the characterization of their physical, chemical, thermal, and mechanical properties (Scheme 1).

Preparation of TGDDM

TGDDM resin was synthesized by reacting 576.36 g (6.25 mol) of epichlorohydrin (ECH) and 93.8 g (0.47 mol) of 4,4′-diaminodiphenyl methane in the presence of 40% aqueous sodium hydroxide solution (113.7 g, 2.84 mol). Excess ECH was removed by distillation (Scheme 1a).
Yield: 160 g (70%) and EEW: 108 (theoretical value: 105).

Preparation of GMP

An amount of 41.3 g (0.33 mol) of 4-methoxy phenol was reacted with 59.2 g (0.64 mol) of ECH in the presence of 40% aqueous sodium hydroxide solution (20 g, 0.5 mol) (Scheme 1b).
Yield: 50% (30.2 g) and EEW: 185 (theoretical value: 180).

Preparation of 1,4-[di-(4-cyanato-diphenyl-2,2′-propane)]-terephthalate (DCDPT)[19]

The preparation of DCDPT involves the following two steps.

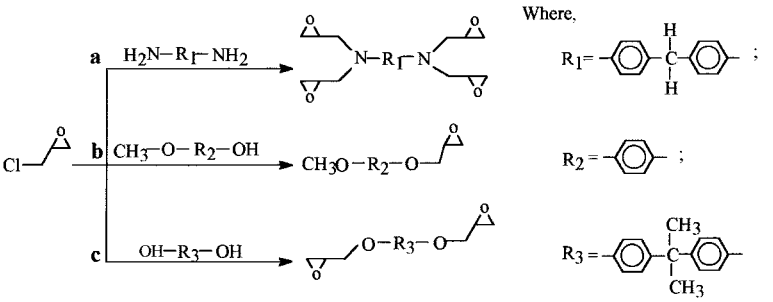
(i) Preparation of 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)]-terephthalate (DHDPT): A measure of 75 g (0.33 mol) bisphenol-A was reacted with 26.7 g (0.132 mol) of terephthaloyl chloride in the presence of 29.23 g (0.29 mol) triethylamine. The product was characterized by FTIR and ^{1}H-/^{13}C-NMR techniques. The number of hydroxyl groups was analyzed by the method described.[20,21]
OH number: theoretical 2.35; experimental: 2.16; % conversion: 92.

(ii) Preparation of DCDPT: An amount of 34 g (0.058 mol) DHDPT was reacted with 12.28 g (0.115 mol) of cyanogen bromide in the presence of 12.89 g (0.128 mol) triethylamine. The reaction was carried out at 0–5°C in acetone medium. The product was isolated with 1 : 1 water/methanol mixture. The product was a white crystalline solid with 70% yield (25.83 g) and a melting point of 129°C (Scheme 2a).

Preparation of the phenoxy polymer involves three steps. In the first step, diglycidyl ether of bisphenol-A (DGEBA) was synthesized. In the second step, DHDPT was synthesized. In the third step, DGEBA was reacted with DHDPT in the presence of imidazole as catalyst to obtain the polymer.

Step 1—Synthesis of diglycidyl ether of bisphenol-A (DGEBA)[22]: The DGEBA resin was synthesized by reacting 33.52 g (0.147 mol) bisphenol-A and 44.84 g (0.485 mol) epichlorohydrin in the presence of 40% aqueous sodium hydroxide 17.64 g (0.44 mol) in isopropyl alcohol as a solvent (Scheme 1c).
Yield: 41.2 g (85%) and EEW: 182 (theoretical value: 176).

Step 2—Preparation of DHDPT: The synthetic procedure is same as given in the preparation of DCDPT.
OH number: theoretical: 2.35; experimental: 2.16; % conversion: 92.



Scheme 1 Synthesis of epoxy resins: Reaction of epichlorohydrin with (a) diaminodiphenyl methane; (b) 4-methoxy phenol; and (c) bisphenol-A..

Step 3—Phenoxy polymer [poly 1,4-(4-glycidyloxy diphenyl-2,2′-propane)]-terephthalate-4,4′-diglycidyloxy diphenyl-2,2′-propane: This was synthesized by reacting 25 g (0.04 mol) DHDPT with 14.5 g (0.04 mol) DGEBA in the presence of 2.9 g (0.042 mol) imidazole. The mixture was dissolved in 50 mL dimethyl formamide (DMF) and heated in an oil bath at 120°C with continuous stirring for 10 h. Then, the solution was poured in ice-cold water. The product was precipitated, filtered, and dried (Scheme 2b). The yield was 30.5 g (80%) and the melting point was 53°C

RESULTS AND DISCUSSION

Characterization of TGDDM and GMP epoxy resins by FTIR

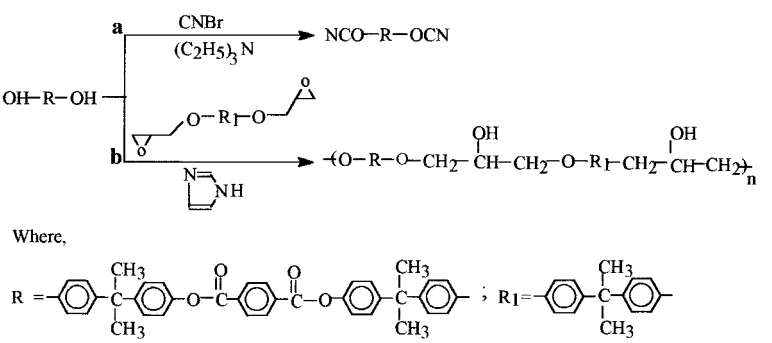
The standard epoxy resins, namely TGDDM and GMP, were synthesized in the laboratory and characterized by FTIR analysis. The product formation of TGDDM and GMP were confirmed by the identification of characteristic absorption peaks [Fig. 1(a, b)]. An asymmetric stretch of the epoxy ring was observed at 925 cm^{-1} for TGDDM and 900 cm^{-1} for GMP. The absorption band at 3016 and 2933 cm^{-1} were due to the aromatic C—H stretch of TGDDM and GMP. The C—C aromatic ring stretch has been identified at 1516 and 1613 cm^{-1} for TGDDM and 1609, 1456, and 11,462 cm^{-1} for GMP, respectively. The C—N stretching of the aromatic amine at 1382 cm^{-1} for TGDDM was observed and the asymmetric and symmetric C—O—C stretch for ethers were also observed at 1231 and 1042 cm^{-1}.

Characterization of cyanate ester resin by FTIR

The FTIR of cyanate ester resin [Fig. 1(c)] shows that a broad doublet peak between 2236 and 2270 cm^{-1} confirmed the formation of the cyanate ester group. The ester carbonyl group absorption was observed at 1736 cm^{-1} frequency, whereas the C—O of ester was at 1071 cm^{-1}. The 1,4-substitution of aromatic ring, aromatic —CH, and —C═C— vibrations were seen around 831, 2811–2968, and 1593–1631 cm^{-1}, respectively. The characteristic doublet peak for isopropyl group vibration absorption was observed between 1350 and 1384 cm^{-1}.

Characterization of phenoxy polymer by FTIR spectroscopy

Figure 2(a) shows the absorption spectra of phenoxy polymer. Aromatic C—H stretch showed a peak at 2965 cm^{-1}. A peak at 1737 cm^{-1} was attributed to the C═O stretch for the ester in conjugation with the phenyl group. The doublet peak of the isopropyl group was observed at 1364 cm^{-1}. The peaks at 1607, 1507, and 1462 cm^{-1} were attributed to the C═C ring stretch. The para-substituted benzene showed a peak



Scheme 2 Synthesis of (a) dicyanate ester and (b) phenoxy polymer.

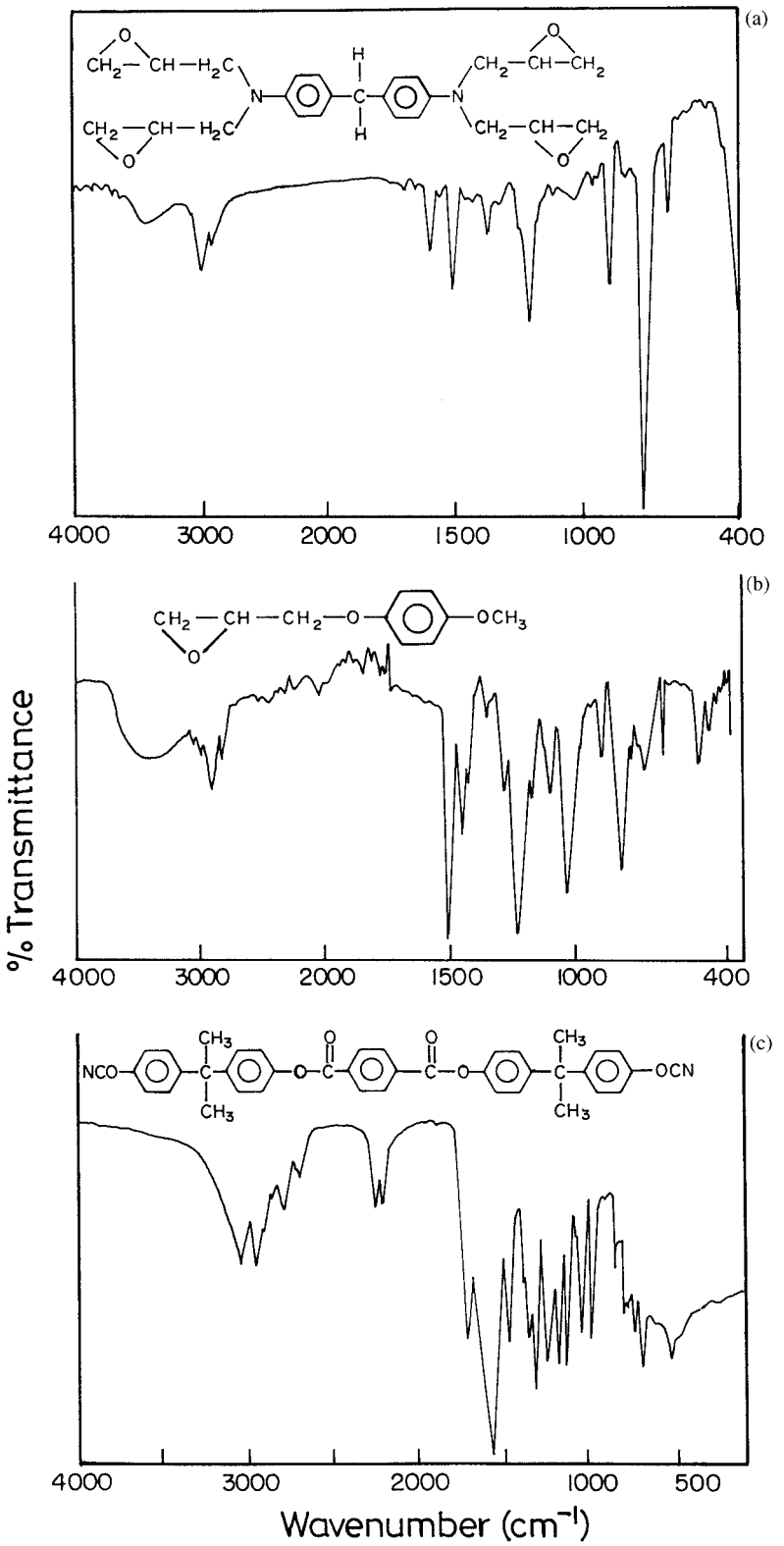


Figure 1 FTIR of (a) TGDDM, (b) GMP, and (c) DCDPT.

at 830 cm^{-1}. The C—O stretch for esters showed a strong absorption at 1071 cm^{-1}. The broad peak at 3444 cm^{-1} was due to the intermolecular hydrogen bonding. Out-of-plane bending in the phenolic group was observed at the 724 cm^{-1} region. The C—O absorption for saturated secondary alcohol was noted at 1170 cm^{-1}. The peak at 900 cm^{-1} for —CH of epoxy and ring breathing of epoxy at 1231 cm^{-1} were miss-

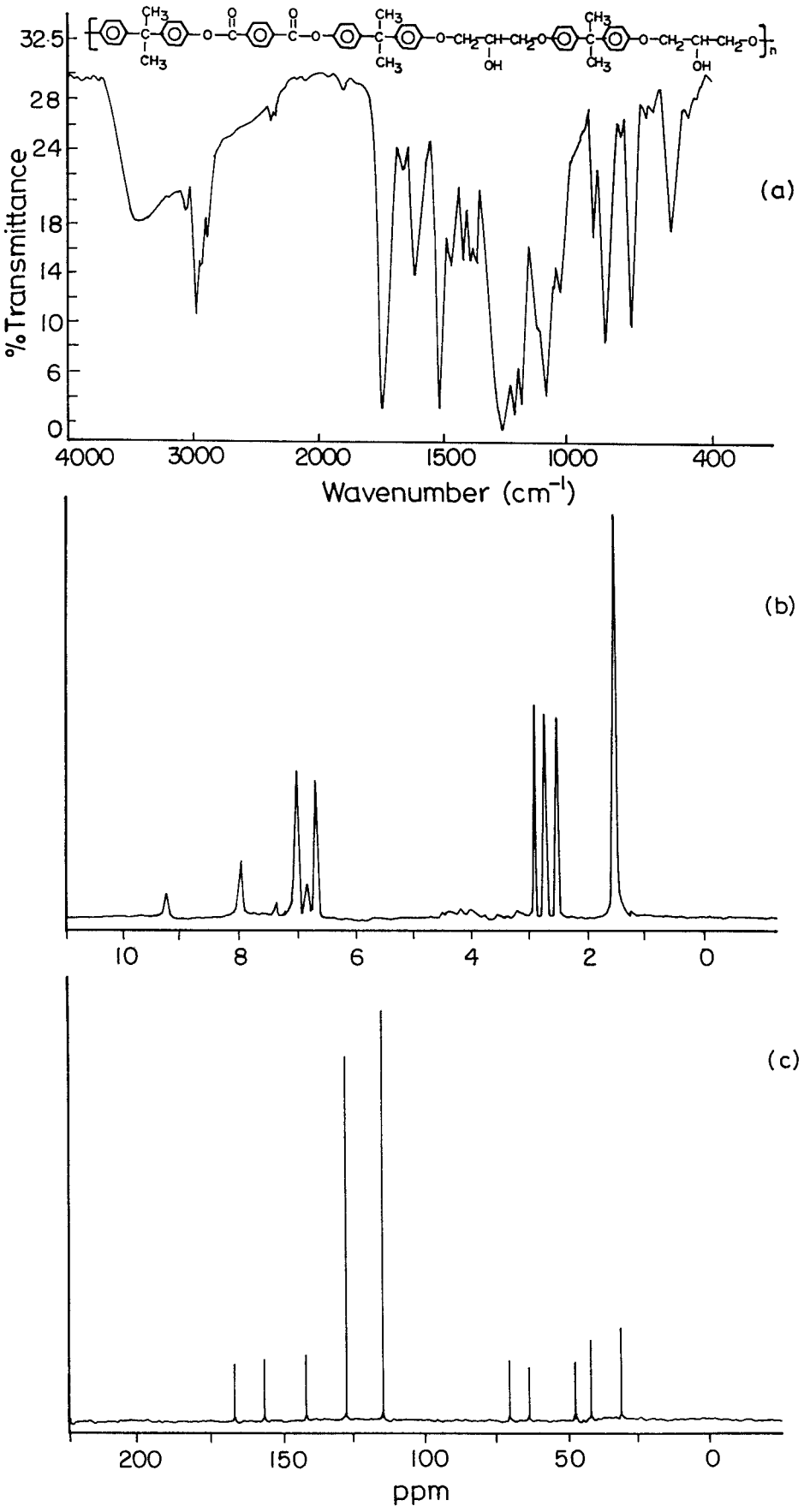


Figure 2 (a) FTIR, (b) ^{1}H-NMR, and (b) ^{13}C-NMR of phenoxy polymer.

ing, which showed the product phenoxy polymer had been formed.

^{1}H-NMR

Figure 2(b) reveals the proton NMR of phenoxy polymer. The resonance signal between 6.6 and 8.0 ppm was due to the aromatic protons. The protons of the —OH group were observed at 9.1 ppm. The isopropyl group showed a signal at 1.52 ppm. The epoxy group showed signals at 2.5–2.8 ppm.

^{13}C-NMR

The ^{13}C-NMR of phenoxy polymer [Fig. 2(c)] showed a signal for aromatic carbons around 113–154 ppm. The carbonyl carbon of the ester showed a peak at 164 ppm. The isopropyl carbons of these showed peaks at 30 and 45 ppm. Epoxy carbonyls showed signals for CH_2—O and CH—O at 41, 63, and 68 ppm, respectively.

Molecular weight determination by GPC

The molecular weight of the phenoxy polymer obtained from GPC indicates that the weight-average molecular weight ($\bar{M}_w$) is 12,381, which is 1.4 times that of the number-average molecular weight ($\bar{M}_n$) of 8845 [i.e., polydispersity ($\bar{M}_w/\bar{M}_n$) = 1.4].

Characterization of modified neat resin castings

TGA

Thermal stability was assessed by TGA. TGA curves for cyanate ester homopolymer (I), phenoxy polymer (II), and for the blends (III, IV, and V) are shown in Figure 3(a–e). The corresponding thermal data for the systems (I–V) are listed in Table II. The 10% weight loss, which is the crude index of the thermal stability of the material, is presented in the table. The new cyanate ester homopolymer (I) shows the highest thermal stability. The phenoxy polymer exhibits a similar decomposition temperature range as that of cyanate ester homopolymer and this may be due to the presence of terephthalates in both systems. Among all the blends, cyanate ester modified blend (IV) shows slightly higher thermal stability than GMP-modified TGDDM/DDS system (III), because of less crosslinked structure of cyanurate rings. Phenoxy polymer modified blend shows higher (254°C for 10% weight loss) temperature, indicating better thermal stability, which may be due to the increased reactive moieties available through the added constituents that form more dense crosslinking network structure in the system.

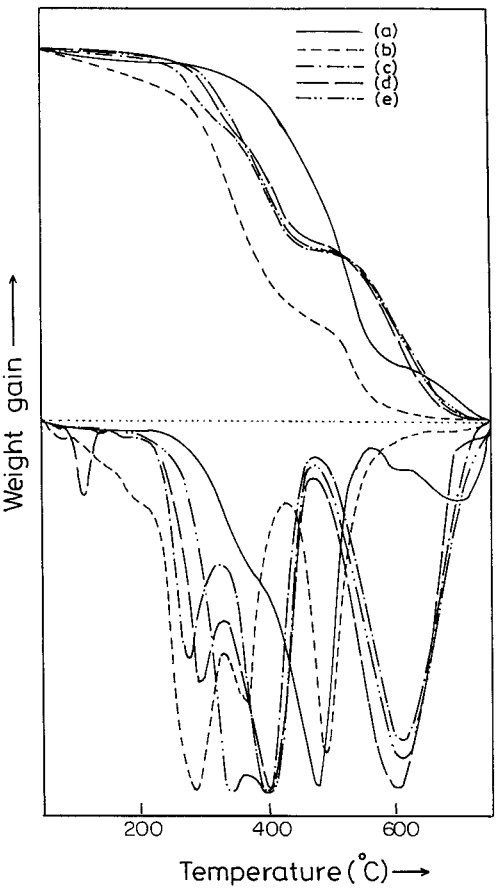


Figure 3 TGA curves of systems (a) I, (b) II, (c) III, (d) IV, and (e) V.

Differential scanning calorimetry (DSC)

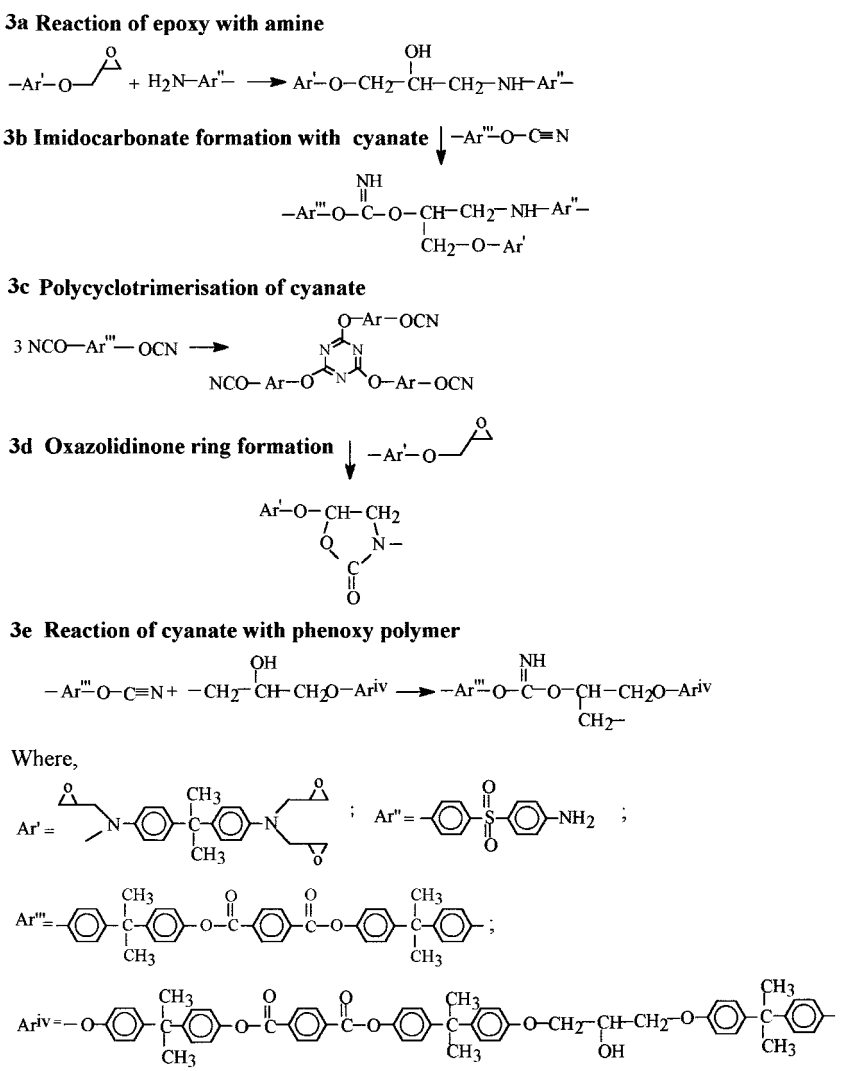
The DSC thermograms of the systems IV and V exhibit three significant exothermic peaks, which indicate the occurrence of complex interactions between the components. The nonisothermal curing behavior of the systems resulted in wide exotherm peaks. The onset of the first exotherm peak observed around 146°C in system IV and around 126°C in system V seems to be the representation of the trimerization of new cyanate ester which is closely comparable with bisphenol-A cyanate ester's exotherm at 135°C.[23] The curing behavior of the systems seems to be similar because each transition temperature of the modified system (V) resembles the unmodified system (IV). The maximum curing temperature of the modified system (V) is 10°C higher than the unmodified system (IV). This may be due to the inclusion of toughener, which also has rigid terephthalate backbone units that enhance the thermal stability of the polymer.

The polycyclotrimer formation of cyanate is a completely random reaction[24] and is complicated because many side reactions are possible.[25] Indeed, the complexity of curing reaction increases with the type and the number of functionality of the components

TABLE II
Thermal Decomposition Data of Cyanate Ester (I) and Phenoxy (II) Homopolymers, and Blended Formulation Systems (III–V)

System	IDT(°C)	% Weight loss of the polymers					Maximum decomposition temperature (°C)	Decomposition temperature range(°C)	Char yield (wt %)
		10	30	50	60	80			
I	200	325	392	441	448	475	451	200–575	0.4
II	192	283	338	391	417	525	315	192–550	8.4
III	175	243	291	418	579	607	392	175–629	6.2
IV	196	246	367	438	550	600	400	196–645	3.6
V	200	254	275	407	575	611	337	200–628	5.8

(Scheme 3). The possible major curing reactions are as follows: reaction of epoxy with amine, cyanate with epoxy hydroxyl, cyclotrimerization of cyanate, oxazolidone ring formation by the rearrangement reaction of trimer with epoxy, and cyanate with phenoxy hydroxyl. Apart from these reactions, there are also possibilities of aromatic amine reacting with cyanate to form adduct which would further degrade thermally to phenol and cyanamide.[26] Also, the epoxy hydroxyls from the reaction of epoxide with amine undergoes nucleophilic substitution reaction with cyanate to give adducts which would further undergo cleavage to give phenol. Thus, the phenols obtained from the adducts may add to cyanate in the presence of a base to



Scheme 3 Possible cure reactions of epoxies with amine, dicyanate, and phenoxy polymer.

TABLE III
Mechanical Properties of the Modified Neat Resin Castings

Resin system	Tensile strength (mPa)	Flexural strength (mPa)	% Elongation	Tensile modulus (gPa)	Flexural modulus (gPa)	Impact strength (J/mm^2)	Hardness
III	39.21	61.79	29.67	2.62	3.7	0.30	90–93
IV	48.38	69.15	33.30	3.16	4.2	0.34	93–96
V	47.26	65.83	31.21	3.08	4.0	0.38	91–95

give bisarylimidocarbonates, which would further react with phenols and form cyanurates.[27,28] Thus, the cyanate reaction with amine helps in increasing the T_g of the cured systems. Nevertheless, the structure of the cured product is determined by the rate of reactions and the initial equivalent ratio of the reactions.[29]

Mechanical properties

TGDDM/DDS cured composites are generally known as high-strength materials. These materials show excellent mechanical properties. TGDDM-cured materials are brittle because of their highly dense crosslinked structure. They need to be modified with low functionality epoxies as diluents and/or be toughened with thermoplastics. Considering these criteria for making high-strength materials, three different composites (III, IV, and V) were made, as given in Table I. The mechanical and physical properties were evaluated (Table III).

The tensile and mechanical strength properties of the system III are much lower than the TGDDM/DDS system studied.[30] This may be due to the addition of GMP, which might have reduced the extent of crosslinking owing to the free unreacted (—OCH_3) end.

System IV shows slightly improved properties over system III, and this may be attributed to the inclusion of DCDPT, which has a long rigid aromatic backbone, whereas system V shows higher impact strength of all the systems (III and IV). This may be due to the presence of phenoxy polymer and DCDPT in the 3-dimensional networks. The long-chain rigid-rod aromatic structure of the phenoxy polymer and DCDPT are to some extent responsible for high tensile and flexural properties.

The mechanical properties of all the systems (III–V) were good, whereas the impact strength property is slightly higher in system IV than system III. This could be the result of the formation of less crosslink network structures of DCDPT. Interestingly, the highest T_g observed for system V may be due to the addition of phenoxy polymer.

Chemical properties

The examination of the specimens immersed in H_2O (RT and 85°C) and solvents such as 10% HCl, 10% NaOH, and acetone was done after 24 h. Indeed, there was neither loss in gloss nor change in dimensions. However, the change in weight of the cured specimens was observed and the results are given in Table IV.

The TGDDM/DDS cured systems shows increased water absorption behavior because of the free unreacted amine groups in the cured network. In the case of acetone, the apparent weight gain is less, which is probably due to the extraction of unreacted monomers. On examining the reagents after removal of the samples, no coloration was observed.

SEM analysis

The phase-separation behavioral changes brought about by the inclusion of phenoxy polymer in the laminate system V were studied by SEM analysis and compared with the laminate system IV, which was without phenoxy polymer. The SEM photomicrographs of the fractured surface for the system IV and V are given in Figure 4(a, b). The bright lines that emanate from the crack with the cut edges were observed in system IV [Fig. 4(a)]. The polymer ligament

TABLE IV
Chemical Resistivity of Modified Neat Resin Castings

	% Weight change after 24 h				
	Water				
Resin systems	RT	85°C	10% NaOH	10% HCl	Acetone
III	0.304	0.556	0.260	0.474	0.113
IV	0.377	0.911	0.280	0.347	0.290
V	0.364	0.372	0.195	0.169	0.113

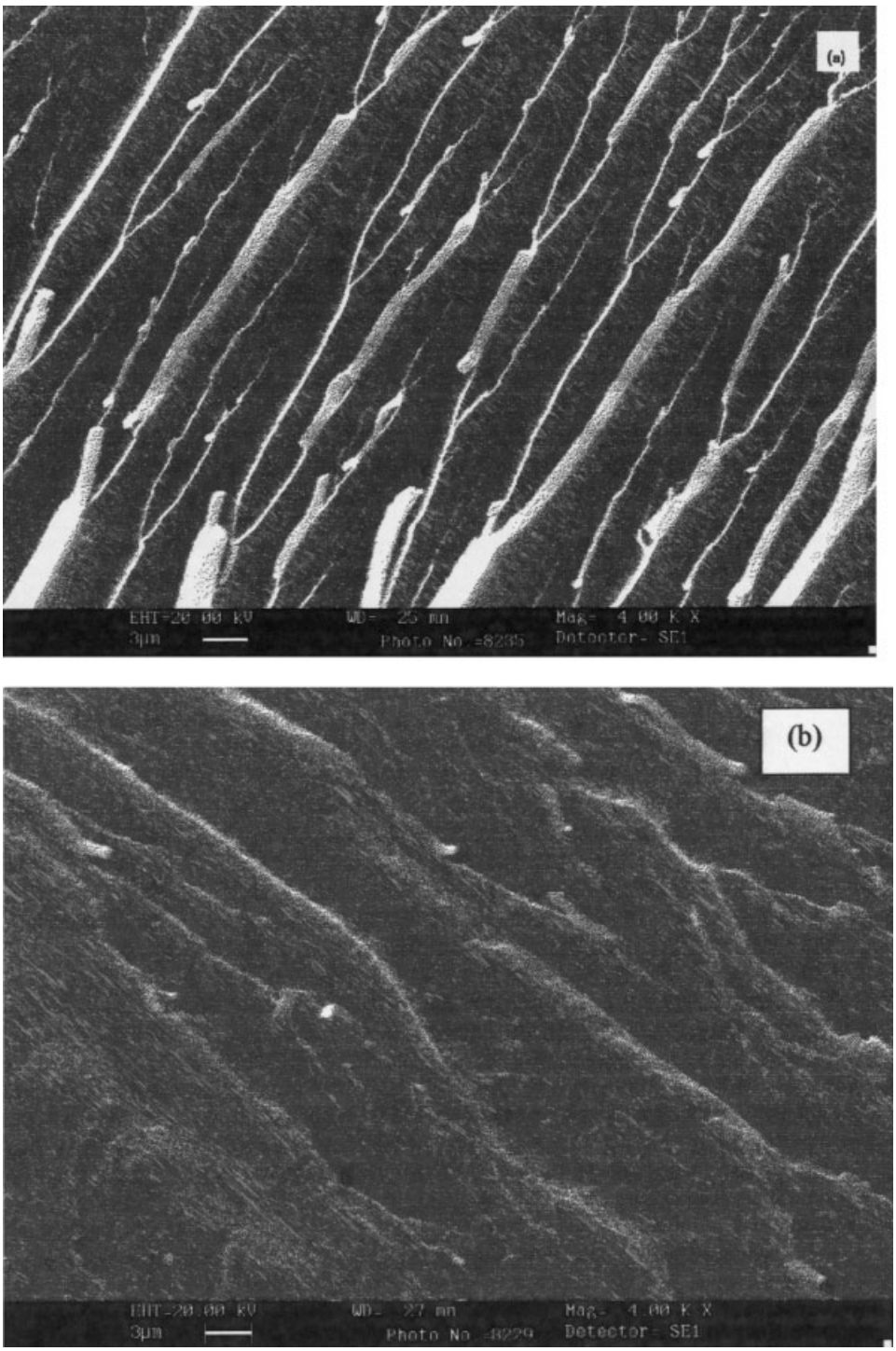


Figure 4 SEM photomicrographs of systems (a) IV and (b) V.

tear appears as straight cuts with sharp edges. This shows that the cured unmodified resin is brittle, whereas for the modified resins, the fractured surface shown in system V [Fig. 4(b)], appears as local shear deformation. Although few definite cut edges were seen at scattered points, the local yielding and shearing seems to be prevalent to some extent.

Both micrographs indicate that the addition of modifiers had no effect on the morphology, and hence, no phase separation was observed. Phase separation occurs only when the epoxy resin possesses different epoxy functionalities. These functionalities exhibit varying kinetics because of the polarity change in the curing of epoxy resins.[31] All the reactants, such as epoxy resins, amine hardener, cyanate ester, and phenoxy polymer, are chemically bonded by the intramolecular reactions; therefore, the chances of phase separation could be ruled out.

The phenoxy polymer used here is miscible with DGEBA epoxy monomer. The structure of phenoxy polymer is similar to DGEBA and is expected to facilitate the compatibility and reduce phase separation. The localized cavitation was also not found in the phenoxy-modified laminate, unlike the rubber-modified system which leads to high-plastic shear yielding in the epoxy system. The SEM of the fractured surface of systems IV and V are similar in their features apart from slight appearance of shear yielding, whereas the cracked surface is slightly blunt in system V when compared to system IV.

CONCLUSIONS

The effect of GMP as a diluent to the TGDDM/DDS system showed low-thermal properties and mechanical strength. This is due to the presence of free (—OCH_3) end groups that remain nonbonded in the network structure, resulting in low crosslinking. Cyanate ester and phenoxy polymer blended with the TGDDM/DDS/GMP system resulted in producing castings having high thermal properties. The increased properties were due to the less dense but thermally stable cyanurate rings formed by cyanates and the presence of rigid terephthalate units in the phenoxy polymer. The SEM analysis of the modified system with phenoxy polymer (V) showed similar features apart from slight appearance of shear yielding with blunt cracked surface when compared with the modified system without phenoxy polymer (IV).

References

1. Bucknall, C. B.; Patridge, I. K. Polymer 1983, 24, 339.
2. Bucknall, C. B.; Patridge, I. K. Polym Eng Sci 1986, 26, 54.
3. Kunz-Donglars, S.; Beaumont, B. W. R.; Ashby, M. F. J Mater Sci 1980, 15, 1109.
4. Yee, A. F.; Pearson, R. A. J Mater Sci 1986, 21, 2462.
5. Sankaran, S.; Chanda, M. J Appl Polym Sci 1990, 39, 1459.
6. Pearson, R. A.; Yee, R. F. J Mater Sci 1986, 21, 2462.
7. Pearson, R. A.; Yee, R. F. J Mater Sci 1986, 24, 2462.
8. Ijima, T.; Tomoi, M.; Sizuki, A. Eur Polym J 1991, 27, 851.
9. Min, B. G.; Hodgkin, J. H.; Stachurski, Z. H. J Appl Polym Sci. 1993, 50, 1065.
10. Akay, M.; Cracknell, J. G. J Appl Polym Sci 1994, 52, 663.
11. Chean, C. S.; Eamor, M. W. Polymer 1995, 36, 2883.
12. Cassidy, P. E. Thermally Stable Polymers; Dekker: New York, 1980.
13. Ellis, B. Chemistry and Technology of Epoxy Resins; Chapman and Hall: New York, 1993, p. 22.
14. Moskala, E. J.; Colaman, M. M. Polym Commun 1983, 24, 206.
15. Robeson, L. M.; Furtek, A. B. J Appl Polym Sci 1979, 23, 645.
16. Shih, W.-C.; Chen-Chim, M. J Appl Polym Sci 1999, 73, 2369–2376.
17. Lee, L. T.; Yang, C. P. J Appl Polym 1992, 991.
18. Schroeder, J. A.; Madsen, P. A.; Foister, R. T. Polymer 1987, 28, 929.
19. Suguna Lakshmi, M.; Reddy, B. S. R. Eur Polym J 2002, 38, 795–801.
20. Malec, E. J.; Christman, R. A. Methods for the Rapid Determination of Hydroxyl Number in Polyesters; Mobay Chem Co., unpublished results.
21. Kline, G. M. Analytical Chemistry of Polymers, Part I; Vol. 12, p. 303; Interscience: New York, 1959.
22. Lee, H.; Neviles, K., Eds. Hand Book of Epoxy Resins; McGraw Hill: New York, 1967.
23. Wang, C.-S.; Lee, M.-C. J Appl Polym Sci 1999, 73, 1611.
24. Bauer, M.; Bauer, T. Polymeric Material Encyclopedia; 1996, Vol. 2 (c), p. 1917.
25. Bauer, J.; Bauer, M. J Macromol. Sci, Chem A 1990, 27, 97.
26. Grigat, E.; Putter, R. Angew Chem Int Ed 1967, 6208.
27. Gupta, A. M.; Macosko, C. W. Makromol Chem, Makromol Symp 1991, 45, 105.
28. Korshak, V. V., J Polym Sci: Polym Chem Ed 1978, 16,1697.
29. Bauer, J.; Bauer, M. Makromol Chem Macromol Sym 1989, 30, 1.
30. Siddaramaiah, K. S. J. J Polym Mater 1996, 13, 223–231.
31. Van Krevelen, D. W. Properties of Polymers; Elsevier: Amsterdam, 1990.