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Synthesis and characterization of new epoxy and cyanate ester resins

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Abstract

New epoxide and cyanate ester resins with an aromatic ester backbone namely 1,3-[di-(4-glycidyloxy diphenyl-2,2′-propane)]-isophthalate (DGDPI) and 1,4-[di-(4-cyanato diphenyl-2,2′-propane)]-terephthalate (DCDPT) were synthesized and the intermediates were characterized by IR, ^{1}H-/^{13}C-NMR spectroscopic methods. The cured products from DGDPI and DHDPI exhibited higher T_g compared with standard epoxy system. The increase in the T_g may be due to the cyanate ester and rigid aromatic backbones present in the curing system. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dihydroxy ester; Diepoxide; Dicyanate ester; Resins; Curing; Thermosetting polymers

1. Introduction

A novel approach to the tailoring of the thermosetting polymers for high performance applications in aerospace industries, printed circuit boards, electrical insulation, adhesives, coatings and microelectronic encapsulation [1–4] involving the preparation of epoxy resins with aromatic ester unit is the subject of current interest.

The standard epoxy resins like tetraglycidyl diamino diphenylmethane, triglycidyl ether of p-aminophenol are known to give network polymers with high glass transition temperatures (T_g). But, high levels of crosslinking makes them very brittle.

It is well known that the polyaromatic ketones, aromatic ethers and polyarylates have good thermal and mechanical properties [5,6]. Hence, these thermoplastic polymers are added in general to the epoxy formulations to improve the properties. However, these polymers show poor solubility in organic solvents leading to difficulties in the processing. In order to incorporate the excellent properties of these thermoplastic polymers to the thermosetting resin, the thermoplastic units were introduced to the monomer backbone. Thus, the epoxy resins with toughening unit will be having process advantage of standard thermoset resin without compromising their thermal properties.

The objective of this study is therefore to synthesize the new epoxide and cyanate ester resins with linear aromatic ester backbone, characterize their properties after curing them together and compared the properties of new epoxy–cyanate system with the standard epoxy–cyanate system.

2. Experimental

2.1. Materials

Bisphenol A, epichlorohydrin, triethylamine, sodium hydroxide and cyanogen bromide (S.D. Fine chem. Ltd., India.) were used as received. Isophthaloyl chloride and terephthaloyl chloride (Ranbaxy company, India) were purified by distillation under reduced pressure just before use. Triethylamine and acetone were dried over anhydrous calcium chloride and distilled. Bisphenol A was purified by recrystallization. The solvents (benzene,

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chloroform, and methanol) were of commercial grade and used as received.

2.2. Synthesis of dihydroxy ester monomers

2.2.1. Synthesis of 1,3-[Di-(4-hydroxy diphenyl-2,2′-propane)]-isophthalate

Into a flask fitted with a mechanical stirrer, nitrogen inlet, dropping funnel containing 142.5 g (0.62 mol) bisphenol A in 150 ml chloroform and stirred. To that 55.55 g (0.55 mol) triethylamine was added dropwise while maintaining the temperature at 0 °C. A solution of isophthaloyl chloride 50.75 g (0.25 mol) in 100 ml of chloroform was added dropwise to the reaction mixture. After the complete addition of terephthaloyl chloride solution, the reaction continued for another 2 h with stirring at 0 °C. The excess chloroform was distilled off under pressure. The residue was poured into excess cold water. The white solid was precipitated, filtered and dried. The product was recrystallized from a mixture of methanol and water (1/1, v/v). White solid product was obtained and the yield was found to be 115 g (78%).

The product was characterized by FT-IR and $^{13}C/^{1}H$-NMR techniques. The presence of the two hydroxyl groups on both the ends was analyzed by the method described [7,8]. OH number: theoretical: 2.35; experimental: 2.16 and % conversion: 92.

2.2.2. 1,4-[Di-(4-hydroxy diphenyl-2,2′-propane)]-terephthalate

190 g of bisphenol A (0.83 mol) was reacted with 67.6 g (0.33 mol) of terephthaloyl chloride in the presence of 74.0 g (0.73 mol) triethylamine. The synthetic procedure adopted for the preparation of 1,3-[di-(4-hydroxy diphenyl-2,2′-propane)]-isophthalate (DHDPI) was similar to the procedure as given in Section 2.2.1. OH number: theoretical: 2.35; experimental: 2.16 and % conversion: 92.

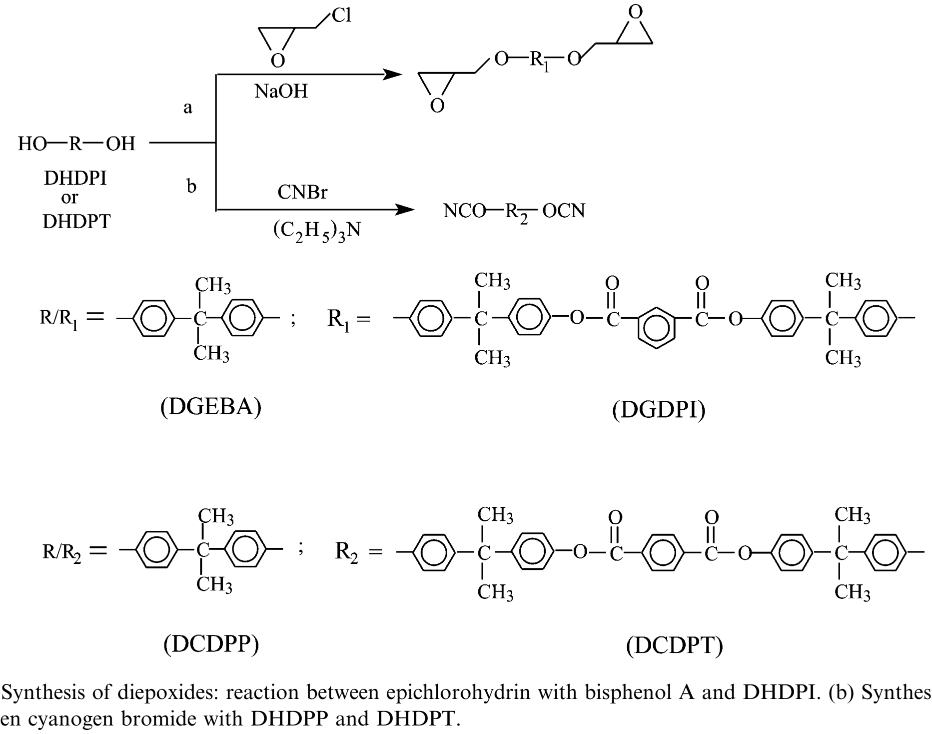
2.3. Synthesis of diepoxides

2.3.1. Synthesis of diglycidyl ether of bisphenol A [9]

The diglycidyl ether of bisphenol A (DGEBA) resin was synthesized by reacting 83.8 g (0.37 mol) bisphenol A and 270 g (2.9 mol) epichlorohydrin in the presence of 40% aqueous sodium hydroxide 37 g (92 ml) in isopropyl alcohol solvent. The reaction was shown in Scheme 1(a). Yield: 106 g (85%) and epoxy equivalent weight (EEW): 182 (theoretical value 176).

2.3.2. Synthesis of 1,3-[di-(4-glycidyloxy diphenyl-2,2′-propane)]-isophthalate (DGDPI)

To a 146 g (0.25 mol) of dihydroxy ester (DHDPI), 184 g (2 mol) epichlorohydrin was charged and 24.9 g (0.62 mol) of sodium hydroxide was added as a 40% aqueous solution, stirred at 70 °C for 2 h and the mixture was then cooled. The reaction mixture was washed



Scheme 1. (a) Synthesis of diepoxides: reaction between epichlorohydrin with bisphenol A and DHDPI. (b) Synthesis of dicyanates: reaction between cyanogen bromide with DHDPP and DHDPT.

several times with distilled water to remove the residual sodium chloride and excess reagents. The product was extracted with benzene and dried under vacuum to evaporate the benzene. The product was a colorless semisolid gave yield 78.3 g (45%). The presence of epoxy groups are confirmed by IR and NMR methods. The reaction was shown in Scheme 1(a). Yield: 78.3 g (45%) and EEW: 354 (theoretical value 349).

2.4. Synthesis of dicyanates

2.4.1. Synthesis of 4,4′-dicyanato diphenyl-2,2′-propane [10]

A batch scale of 100 g cyanate ester was synthesized by the reaction of 74.6 g (0.7 mol) cyanogen bromide with 81 g (0.35 mol) bisphenol A in the presence of 90 g (0.89 mol) triethylamine as a catalyst at 0 °C.

In a three necked flask equipped with a mechanical stirrer, and a nitrogen inlet containing a cooled solution of bisphenol A and cyanogen bromide in acetone, triethylamine was added dropwise with a continuous stirring in an ice bath. After complete addition of the catalyst, the reaction mixture was stirred for a further period of 1 h while maintaining the ice bath temperature at 0 °C and filtered under vacuum. The precipitate was washed with acetone and filtered. The filtrate was poured into cold distilled water to precipitate the bisphenol A cyanate ester from the solution. The crude product was further purified by recrystallization in methanol:water (1:1 v/v). The product was a white crystalline with 76 g (80% yield) and m.p. 75–78 °C. The reaction was shown in Scheme 1(b).

2.4.2. Synthesis of 1,4-[di-(4-cyanato diphenyl-2,2′-propane)]-terephthalate

1,4,-[di-(4-cyanato diphenyl-2,2′-propane)]-terephthalate (DCDPT) was synthesized by a procedure analogous to the synthesis of 4,4′-dicyanato diphenyl-2,2′-propane (DCDPP). The product obtained was white crystalline and had a melting point around 129 °C. The yield was 68%. The reaction was shown in Scheme 1(b).

2.5. Curing method of diepoxides with dicyanate esters

The diepoxides and dicyanate esters were blended by employing the compositions given in Table 1. Sixty parts of epoxy and 40 parts of cyanate esters were thoroughly mixed at 70 °C to get a homogeneous liquid. When the samples were melted and became homogeneous, then these were transferred to aluminum foil cups and deaerated under vacuum for 0.5 h at 70 °C to drive the air bubbles in the formulations [11]. All the formulations were heated to 180 °C slowly and kept for 2 h. Then raised the temperature to 200 °C and kept for 2 h. The reaction was shown in Scheme 2.

2.6. Characterization

2.6.1. IR spectroscopy

Nicolet FT-IR Spectrometer model 20 DXB was used for studying the IR spectroscopy (400–4000 cm^{-1}) of monomers and cured samples. Solid KBr pellets were prepared for crystalline compounds. Liquid samples were done using a liquid cell.

2.6.2. ^1H and ^{13}C-NMR spectroscopy

^1H and ^{13}C-NMR of the compounds synthesized were run on a Bruker 320 MHz spectrometer at room temperature using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard.

2.6.3. Thermal analysis

Differential scanning calorimetric (DSC) analysis was performed using a Du Pont 200 microthermobalance. The heating rate for DSC was 10 °C/min in the nitrogen atmosphere.

2.6.4. Thermogravimetric analysis

Thermal properties of the formulation C and D were investigated on Mettler 3000. The thermogravitmetric analysis were carried out at the rate of 10 °C/min.

3. Results and discussion

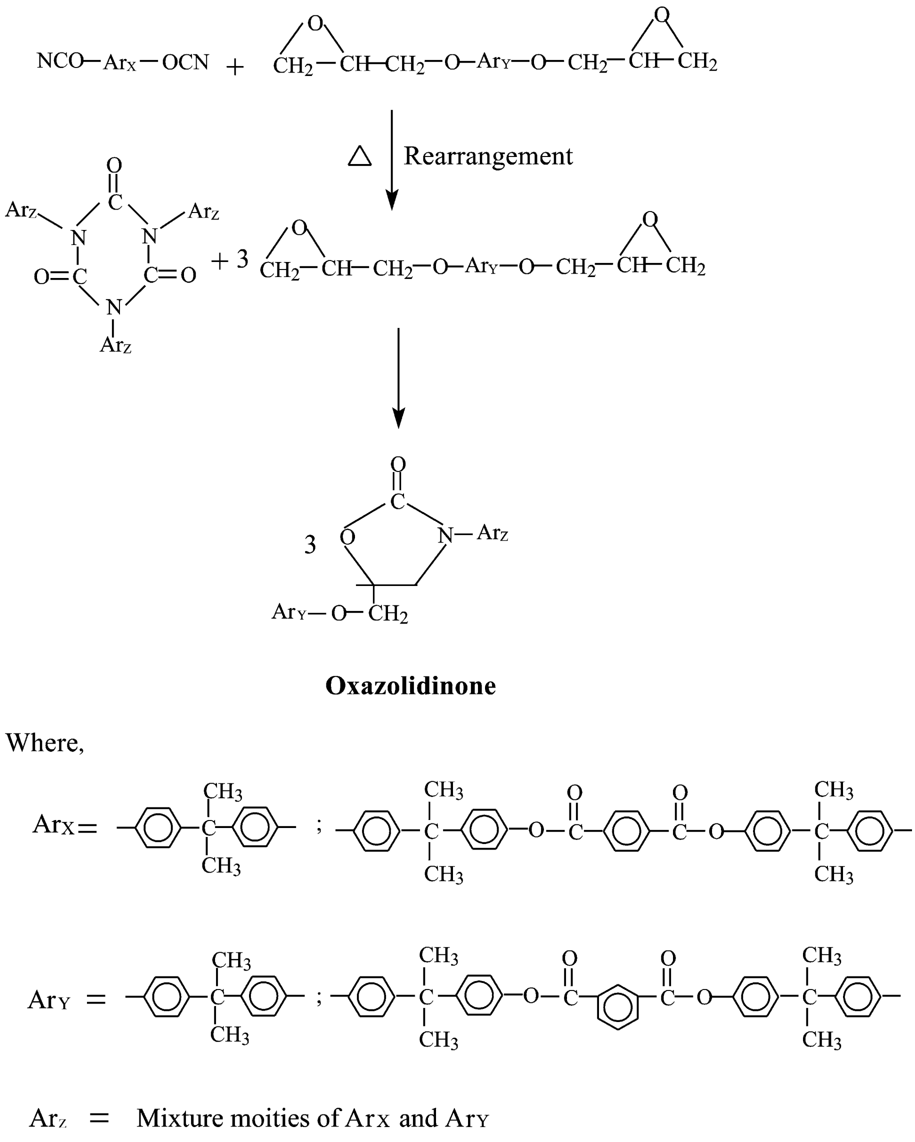
3.1. Characterization of dihydroxy esters (DHDPT and DHDPI)

3.1.1. Infrared spectroscopy of dihydroxy esters

IR spectra of dihydroxy esters show that the dihydroxy ester formation was confirmed by the appearance of broad spectrum around 3500 cm^{-1} for OH

Table 1
Formulation data and T_g values

Formulation	Epoxy	Cyanate	IDT (°C)	Decom. range (°C)	Temp (°C) at different % weight loss of polymer				T_g (°C)
					40	60	80	90	
A	DGEBA	DCDPP	–	–	–	–	–	–	225
B	DGDPI	DCDPP	333	333–700	360	465	535	570	177
C	DGDPI	DCDPT	348	348–626	375	430	540	580	260



Scheme 2. Curing reaction between dicyanate and diepoxide resins.

group, and a characteristic peak around 1700 cm^{-1} for ester carbonyl group.

3.1.2. ^{1}H-NMR spectroscopy of dihydroxy esters

The ^{1}H-NMR spectra of all the dihydroxy esters were studied. The chemical shift value for the OH group was observed in the order $8.3 < 9.1$ for $I(b) < I(a)$ respectively, due to the stiffness of the molecular backbone of the compounds.

3.1.3. ^{13}C-NMR spectroscopy of dihydroxy esters

The ^{13}C-NMR spectra of the esters show the resonance corresponding to all the carbons present in the compound. The characteristic chemical shifts of ^{13}C-NMR data was given Table 2.

3.2. Characterization of diepoxides

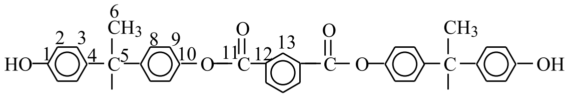
3.2.1. IR spectral analysis of diepoxides

The standard epoxy resin namely DGEBA was synthesized in the laboratory by reacting bisphenol A with epichlorohydrin. This resin was used for comparison with other resins.

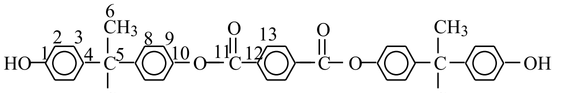
Similarly the epoxidation of DGDPI (Fig. 1a) compound was confirmed by the identification of characteristic absorption peaks. The ester –CO– was seen at 1722 cm^{-1}. The epoxy ring C–H vibration frequency was

Table 2
^{13}C-NMR spectral data of dihydroxy esters

Aromatic dihydroxy ester	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}
DHDPI	153	114	127	148	42	31	42	130	14	143	164	148	133
DHDPT	155	114	127	141	41	30	140	133	114	140	165	154	129



DHDPI



DHDPT

observed at 915 cm^{-1}, while the appearance of peaks between 2800–3000 cm^{-1} for aromatic –CH– are predominant. The absence of the absorption of OH group indicates the conversion of OH group into the corresponding epoxy group.

3.2.2. ^{1}H-NMR spectra of diepoxides

^{1}H-NMR spectrum of DGDPI (Fig. 1b) shows a singlet at 1.6 ppm for the isopropylidine protons and the epoxy propyl protons of O–CH$_2$, CH, CH$_2$ were seen at 3.3, 4.3, 6.7 ppm and aromatic protons were observed around 7.3 ppm.

3.2.3. ^{13}C-NMR spectra of diepoxides

The ^{13}C-NMR spectra of DGDPI is shown in Fig. 1(c). The aliphatic carbons representing the epoxy group are observed in the region 41–70 ppm. The ester carbonyl which is present in both the systems is seen at 165 ppm. The aromatic carbons are mostly seen around 113–156 ppm. The characteristic carbon atoms of the isopropyl group are observed at 30 and 45 ppm.

3.3. Characterization of dicyanate ester resin (DCDPP and DCDPT)

3.3.1. IR spectroscopy of dicyanate ester resin

The FT-IR analyses were carried out for both the DCDPP and DCDPT (Fig. 2a). The broad doublet peak observed between 2236–2273 and 2236–2270 cm^{-1} are due to the –OCN vibration absorption of DCDPP and DCDPT. Another doublet peak is observed between 1351–1383 and 1350–1384 cm^{-1} are due to the presence of isopropyl group vibration absorption of DCDPP and DCDPT. The 1,4-substitution of aromatic ring is seen at 831 cm^{-1} for both the cyanate esters. The ester carbonyl group absorption frequency is seen at 1736 cm^{-1} for DCDPT. The C–O of ester is seen at 1071 cm^{-1}. The aromatic –CH, and –C=C– vibrations are seen around 2811–2968 and 1593–1631 cm^{-1} region.

3.3.2. ^{13}C-NMR spectroscopy of dicyanate ester resin

The characteristic absorptions at 151 and 150.9 ppm confirm the formation of OCN group in DCDPT (Fig. 2c). The aromatic carbons and isopropyl carbons are observed around 114–154 and 29.5–42.5 ppm. The ester carbon seen at 164.3 ppm for DCDPT.

All these IR, ^{1}H- and ^{13}C-NMR spectral analyses confirm the synthesized compounds of diesters, diepoxies and dicyanate ester resins.

3.4. Formulation

The new DGDPI resin cured with DCDPP (formulation B) exhibit good T_g, around 177 °C. But inferior to the T_g value of DGEBA–cyanate (formulation A). On the other hand, DGDPI cured with DCDPT (formulation C) displays very high T_g around 260 °C. The rigid aromatic cyanate ester backbone which influences for the high T_g of the formulation C.

3.5. DSC analysis of diepoxides cured with dicyanate ester resins

Polycyclotrimerization i.e., the formation of cyanurate ring system by the polymeric condensation of three aromatic cyanate groups to form the crosslinked aromatic ring system is a completely random reaction [12] and it is a quite complicated since many reactions are possible [13]. The complexity of curing reaction

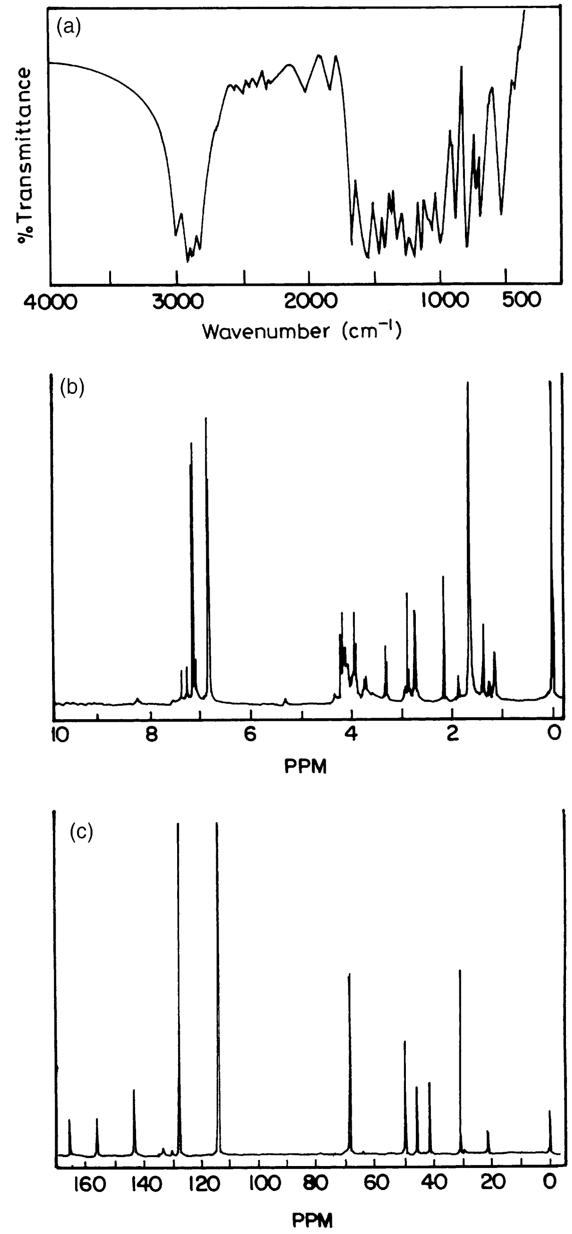


Fig. 1. (a) IR, (b) ^{1}H-NMR and (c) ^{13}C-NMR spectra of DGDPI.

increases with increasing functionality of the cocured epoxy resins. The structure of the cured products will depend on the rate of each reaction and the initial equivalent ratio of the dicyanate ester and glycidyl ether [14]. The extent of curing reaction of cyanate and epoxy resins [15–17] synthesized were analyzed by the DSC analyses and the T_g value of the cured samples are presented in Table 1.

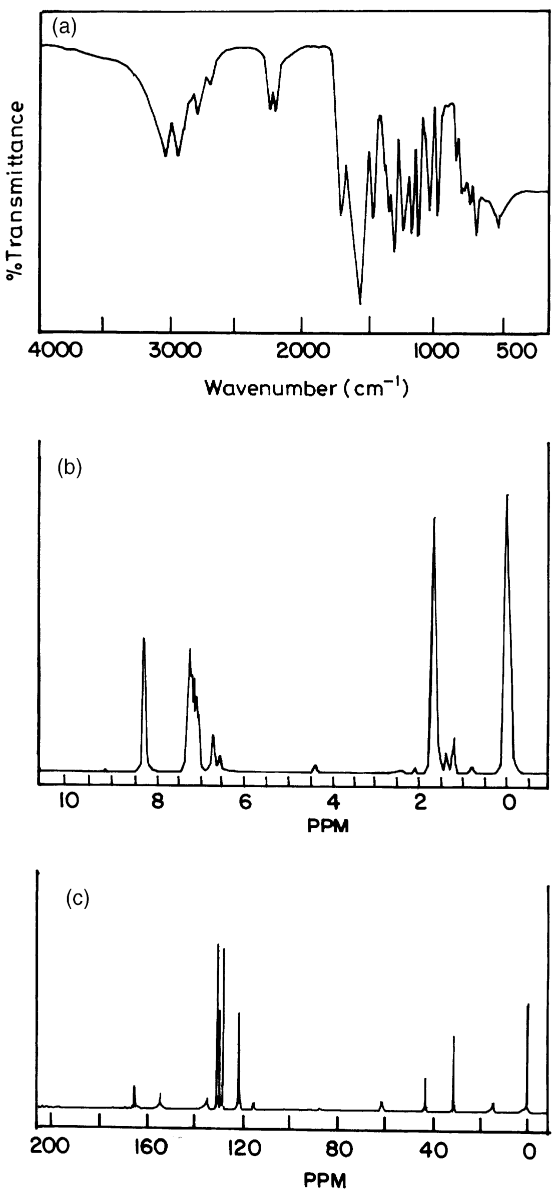


Fig. 2. (a) IR, (b) ^{1}H-NMR and (c) ^{13}C-NMR spectra of DCDPT.

3.6. Thermal stability of the new diepoxide–dicyanate polymers

Thermal properties of the formulation B (DGDPI cured with DCDPP) and the formulation C (DGDPI cured with DCDPT) were investigated by recording the thermograms (Fig. 3) of these systems in air (Table 1).

Both the formulations B and C undergoes two stage degradation. The initial decomposition temperature of the formulation is higher than that of formulation C,

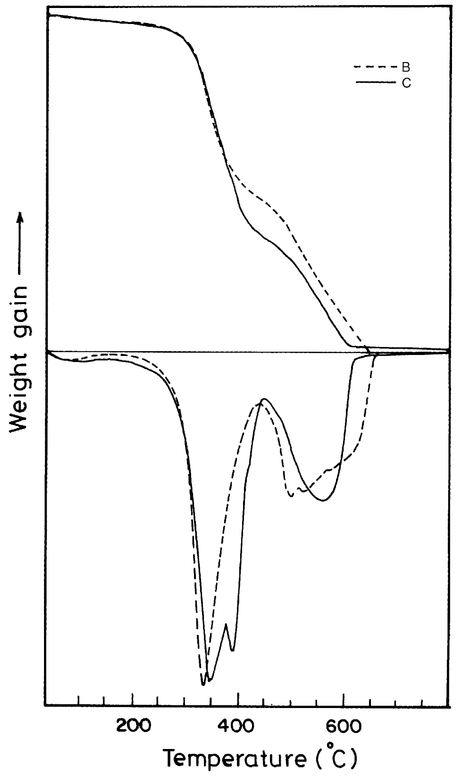


Fig. 3. TGA of formulations B(- - -) and C(—).

while the decomposition range and the percentage weight loss of the polymer are of the same order.

4. Conclusions

The new dihydroxy esters (DHDPI and DHDPT) with aromatic backbone have been synthesized and were characterized spectroscopically. DHDPI was epoxidized with excess of epichlorohydrin to produce DGDPI. DHDPT was reacted with cyanogen bromide to produce dicyanate ester resin, DCDPT. The synthesized diepoxides and dicyanates were analyzed by spectroscopic methods. The epoxy group (EEW) present in diepoxides was estimated quantitatively by titration method. Different formulations were made with diepoxides and dicyanates, and their thermal properties were investigated. The formulation with the new DGDPI and DCDPT shows high T_g and high decomposition temperature range. The high T_g and good thermal stability properties of the system enable its utility in the area of aerospace, electronics, composites and adhesives.

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