

Studies on the curing and thermal behaviour of diglycidyl ether of bisphenol-A (DGEBA) in the presence of aromatic diimide–diacids

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Abstract This paper describes the synthesis and characterization of aromatic diimide–diacids (DIDAS) obtained by reacting pyromellitic dianhydride (PMDA), 4,4'-oxo diphthalic anhydride (ODA), 1,4,5,8-naphthalene tetra carboxylic dianhydride (NTDA) with excess of 4-aminobutyric acid (B) or 6-aminohexanoic acid (H) using *N,N*-dimethyl formamide (DMF) as solvent. The synthesized compounds were used as curing agents to investigate the effect of structure on the curing and thermal behaviour of diglycidyl ether of bisphenol-A (DGEBA). Structural characterization of DIDAS was done by using FTIR, ¹H-NMR, ¹³C-NMR spectroscopy and elemental analysis. Curing behaviour of DGEBA in the presence of aromatic DIDAS was investigated by differential scanning calorimetry (DSC). The peak exotherm temperature (T_p) was low in the case of DIDAS synthesized from ODA and high in the case of DIDAS synthesized from NTDA. Thermal stability of the isothermally cured DGEBA with DIDAS was investigated using dynamic thermogravimetry in nitrogen atmosphere. The char yield was highest for resin cured with DIDAS containing NTDA.

Keywords Char yield · Curing · Imide-acids · Thermal stability

Introduction

Epoxy resins find uses in many industrial applications viz in surface coatings, adhesives, structural insulating materials

for electronic devices because of their good chemical resistance and superior electrical and mechanical properties [1, 2]. However, the conventional known epoxy resins are inefficient to satisfy the required properties in the field of advanced materials, which require high thermal and flame resistance [3–5]. Various attempts have been made to improve thermal stability and flame retardancy of epoxy resins. The properties can be varied by the modification of epoxy backbone, i.e., either at the time of synthesis or during cure using curing agents of varying structures. The curing process in the epoxy resins can be initiated by using a wide range of curing agents such as amines, anhydrides, acids and amino formaldehyde–resins [6–9]. Compounds containing imides group and polymers [10–14] that contain aromatic and/or heterocyclic groups can offer desirable high temperature stability. Polyimide/polyamide-acid endcapped with amines have been used to impart higher thermal stability and flame resistance. Hay et al. [15] studied the moulding of linear unreactive polyimides for toughening of epoxy-diaminodiphenyl sulphone system. They achieved increase in the fracture toughness with no loss of modulus but with little influence on the thermal capability across the range of modifying polyimides. Polyimide endcapped with amine or polyimide-siloxane [16]/polyamide-acid [17, 18] have also been used for the improvement of thermal and chemical resistance of epoxy resin. Aromatic imide–amines were found to impart better thermal stability and flame resistance to epoxy resins [19]. The cyclophosphorus-containing epoxy polymers obtained with *N,N'*-(4, 4'-diphenyl sulfone) bis(trimellitimide) (DIDA) have a higher char yield on pyrolysis than nonphosphorylated epoxy polymers [20]. In recent years, modification of epoxy resins by amine or carboxy terminated liquid poly (butadiene-co-acrylonitrile) has been investigated to improve the toughness [21]. Abraham [22] studied the curing behaviour of epoxy resin with

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diimide-diacid, 2,2-bis[4-(4-trimellitimidophenoxy)phenyl] and it is found to give the best results for improving the wetting behaviour of epoxy resin and also increase the adhesive strength at room temperature as well as at elevated atmosphere. In view of above it was considered worthwhile to study the curing and thermal behaviour of DGEBA by using simple DIDAS as curing agents. In this article, we synthesized DIDAS of varying structure obtained by reacting dianhydrides [pyromellitic dianhydride (PMDA) or 4,4'-oxo diphthalic anhydride (ODA) or 1,4,5,8-naphthalene tetra carboxylic dianhydride (NTDA)] with amino carboxylic acids [4-aminobutyric acid (B) or 6-aminohexanoic acid (H)] and investigated the curing behaviour and resultant thermal stability of diglycidyl ether of bisphenol-A (DGEBA) with synthesized compounds.

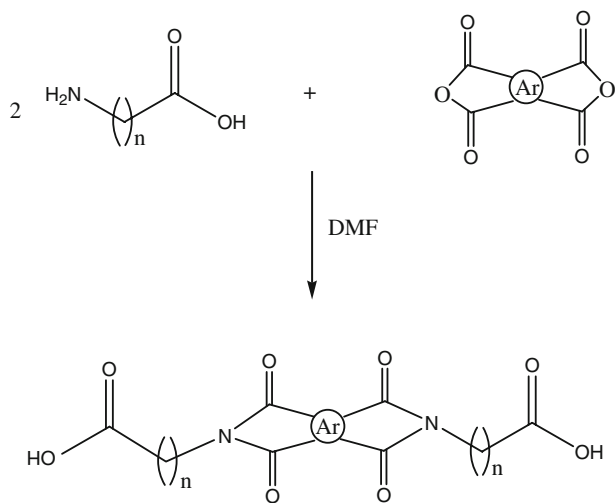
Experimental

Materials

Diglycidyl ether of bisphenol-A (DGEBA, grade LY556, having epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd, PMDA, ODA, and NTDA were all purchased from Aldrich and were used as received. 6-Aminohexanoic acid (H) and 4-aminobutyric acid (B) were purchased from Merck and were used without further purification. *N,N*-dimethyl formamide (DMF) was dried over P_2O_5 and then vacuum distilled. Benzene (Merck) and Ethanol (Qualigen) were used as such.

Synthesis of diimide-diacid (DIDA)

Diimide-diacids [23] were prepared by reacting one mole of dianhydride with excess of aliphatic amino carboxylic acids (app. 2.5 mol), as shown in the reaction Scheme 1.



where

n	Ar	SAMPLE DESIGNATION	FMW
5		PH	444
5		OH	536
5		NH	494
3		PB	388
3		OB	480
3		NB	438

Scheme 1 Reaction scheme for the synthesis of diimide-diacids (DIDAS)

A solution of pyromellitic dianhydride (PMDA) (1 g, 4.58 mmol) in dry *N,N*-dimethyl formamide (DMF) was gradually added into the stirred solution of 6-aminohexanoic acid (H) (1.20 g, 9.17 mmol) in anhydrous *N,N*-dimethyl formamide (DMF) under nitrogen atmosphere and the reaction mixture was refluxed for 2 h. A quantitative amount of dry benzene was added and the reaction mixture was heated up to 170 °C for 2 h. Stoichiometric water produced during the course of the reaction was collected by a Dean-Stark trap. The reaction mixture was then cooled to room temperature and DIDAS was precipitated in ice water and recrystallized from ethanol. It was then dried in the vacuum oven at 80 °C. The yield of the white crude product was app. 85%.

Similarly, all other DIDAS were prepared by reacting H and B with PMDA or NTDA or ODA. The DIDAS were purified by recrystallization in ethanol solution. The DIDAS obtained by reacting PMDA or NTDA or ODA with H or B have been designated as PH/PB, NH/NB, OH/OB, respectively.

Characterization

Structural characterization of DIDAS

Structural characterization of DIDAS was done using FTIR, 1H -NMR and ^{13}C -NMR spectroscopic techniques. Elemental analysis was carried out using EURO EA 3000 elemental analyzer. IR spectra were recorded in KBR pellets using Shimadzu FTIR 8300 spectrophotometer.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker 300 spectrophotometer using DMSO-d_6 as solvent and tetramethyl silane (TMS) as an internal standard.

Curing studies

For curing studies, freshly prepared samples obtained by mixing stoichiometric amounts DIDAS and DGEBA were used for recording DSC traces. For this purpose, known amount of DIDAS was dissolved in a minimum amount of ethyl alcohol, which was then mixed with DGEBA. The epoxy resins cured with stoichiometric amount of DIDAS have been designated by adding a prefix E to the letter designation of DIDAS. For example, DGEBA cured using PH and OH has been designated as EPH and EOH, respectively. DSC scans of freshly prepared DGEBA and DIDAS mixture were recorded using Rheometric analyzer having 910 DSC modules. A heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and a sample weighing $5 \pm 1\text{ mg}$ was used in each experiment. DSC scan of isothermally cured samples were also recorded to determine the effect of network structure on the glass transition temperature.

Thermal stability

Thermal stability of the DGEBA cured isothermally by heating in an air-oven at $200 \pm 20\text{ }^\circ\text{C}$ for 3 h in the presence of DIDAS PH/PB/NH/NB/OH/OB was investigated by recording TG traces in nitrogen atmosphere (flow

rate $60\text{ mL}/\text{min}$) Rheometric thermal analyzer having TG 1500 module was used for recording TG traces. A heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and sample weighing $11 \pm 1\text{ mg}$ was used in each experiment.

Results and discussion

Structural characterization of DIDAS

The DIDAS were of white to light brown in colour. They are soluble in common organic solvents such as DMF, chloroform, etc. The physical characteristics of the DIDAS are given in Table 1. The yields were in the range of 70–89%.

Elemental analysis

Results of elemental analysis are summarized in Table 2. The calculated values of CHN agreed well with the experimentally determined values. Thus, the structure of DIDAS synthesized in the present work was confirmed.

Infrared spectroscopic studies

Figure 1 shows FTIR spectrum of OB DIDAS, respectively. Absorption bands due to imides were observed in all samples at 1770 ± 20 and $1720 \pm 10\text{ cm}^{-1}$, respectively. Stretching bands due to C=O group of carboxylic acids was observed at $1695 \pm 30\text{ cm}^{-1}$. Absorption bands due to C-H and O-H stretch were observed at $2850 \pm 20\text{ cm}^{-1}$ and $2630 \pm 30\text{ cm}^{-1}$. An absorption band due to C-N stretch was observed at $1413\text{--}1467\text{ cm}^{-1}$. The broad peak around $1580\text{--}1660\text{ cm}^{-1}$ implies the C=C stretch in benzene ring. In DIDAS OB and OH, a strong absorption band due to Ar-O-Ar linkage was obtained at 1079 cm^{-1} .

$^1\text{H-NMR}$

In the $^1\text{H-NMR}$ spectrum of DIDAS, a characteristics signal due to $-\text{COOH}$ protons was observed at $\delta 9.6\text{ ppm}$ (triplet)

Table 1 Physical characteristic of diimide–diacids (DIDAS)

No.	Sample designation	Colour	Yield/%
1	PH	Off-white	85
2	OH	Dirty white	73
3	NH	Light brown	82
4	PB	White	78
5	OB	White	74
6	NB	Light brown	89

Table 2 Results of elemental analysis of diimide–diacids (DIDAS)

No	Sample designation	FMW	C (%)	H (%)	N (%)
1	PH	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$	59.27 (59.45)	5.40 (5.40)	6.29 (6.30)
2	OH	$\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_9$	62.62 (62.68)	5.21 (5.22)	5.22 (5.22)
3	NH	$\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_8$	63.17 (63.15)	5.24 (5.26)	5.62 (5.66)
4	PB	$\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_8$	55.67 (55.67)	4.15 (4.12)	7.20 (7.21)
5	OB	$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_9$	60.00 (59.98)	4.11 (4.10)	5.83 (5.83)
6	NB	$\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_8$	60.27 (60.27)	4.10 (4.098)	6.39 (6.39)

Figures in brackets indicate calculated values

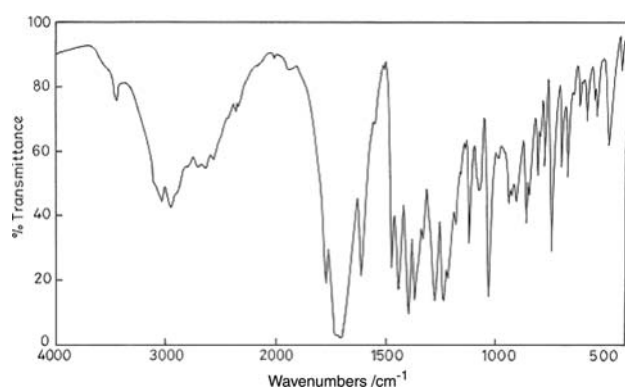


Fig. 1 FTIR spectrum of OB diimide-diacid

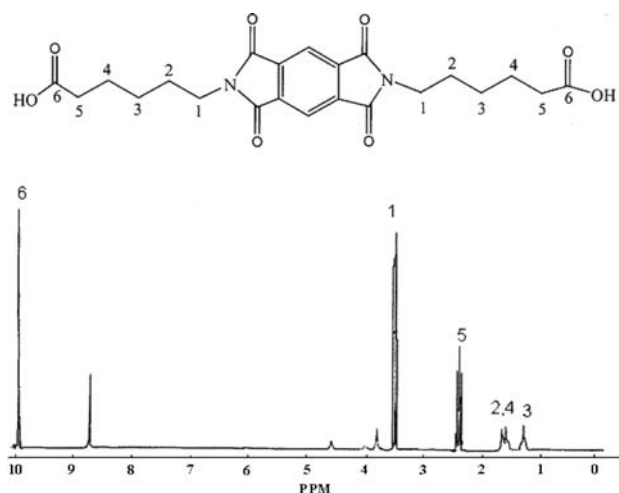


Fig. 2 $^1\text{H-NMR}$ spectrum of PH diimide-diacid

Table 3 $^1\text{H-NMR}$ of PH, diimide-diacid

Type of proton	1	2	3	4	5	6	Aromatic protons
Chemical shifts	3.59	1.58	1.3	1.58	2.32	9.6	8.76
	4H,tr	4H,m	4H,m	4H,m	4H,tr	4H,tr	2H,s

and a multiplet due to aromatic protons was observed in the range of δ 6.8–8.7 ppm. The integration was used to calculate the number of protons. A representative $^1\text{H-NMR}$ spectrum of PH is shown in the Fig. 2 and their chemical shift values are given in the Table 3. The shifts are based on the assigned labels of protons.

$^{13}\text{C-NMR}$

The $^{13}\text{C-NMR}$ spectrum of NH is shown in Fig. 3. These resonance lines in the spectrum fall into three regions, i.e., 20–70 ppm for aliphatic carbons, 110–140 ppm for aromatic Carbons, and 166 ppm for carbonyl carbons of the imide group and 173 ppm for the carbonyl carbon of

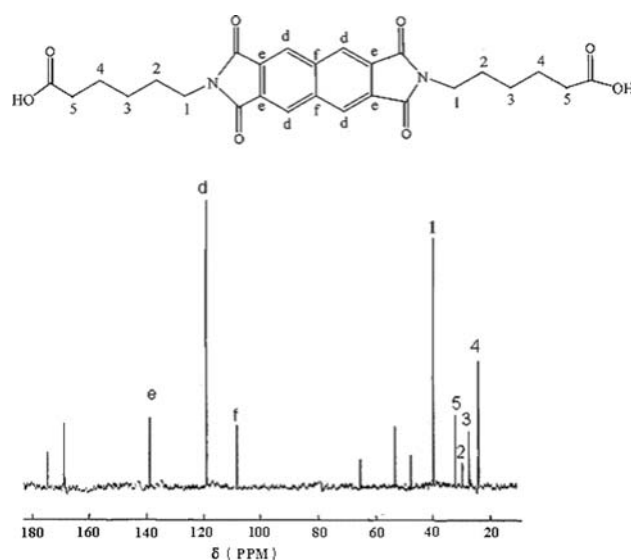


Fig. 3 $^{13}\text{C-NMR}$ spectrum of NH diimide-diacid

Table 4 $^{13}\text{C-NMR}$ of NH, diimide-diacid

Aliphatic carbons				
1	2	3	4	5
39.81	27.45	25.60	23.94	33.11
Aromatic carbons			Carbonyl carbons	
d	e	f	Imide	Carboxylic
117.23	137.04	110.79	166.41	172.73

carboxylic group. The chemical shifts of the characterized carbons of NH are listed in Table 4. These shifts are based on the assigned labels of carbon in Fig. 3.

Curing studies

The effect of structure and molecular size of DIDAS on the curing behaviour was monitored by recording DSC traces. In the DSC scan of DGEBA alone, no exothermic transition was seen in the temperature range of 50–350 °C indicating the absence of curing or cross linking. In the DSC scans of DGEBA in the presence of DIDAS, a broad exothermic transition in the temperature range of 140–195 °C. DSC exotherms were characterized by noting the following temperatures;

T_i	Kick-off temperature, where the curing starts.
$T_{\text{on-set}}$	Temperature where the first detectable heat is released. It was obtained by Extrapolation of steepest portion of curve.
T_p	Temperature of peak position of exotherm.
T_f	Temperature of end of curing exotherm obtained by extrapolation of the end set of the exotherm transition.

Fig. 4 DSC scan of DGEBA in presence of stoichiometric amount of diimide-diacids: **a** OH, **b** OB and **c** PB (heating rate of 10 °C)

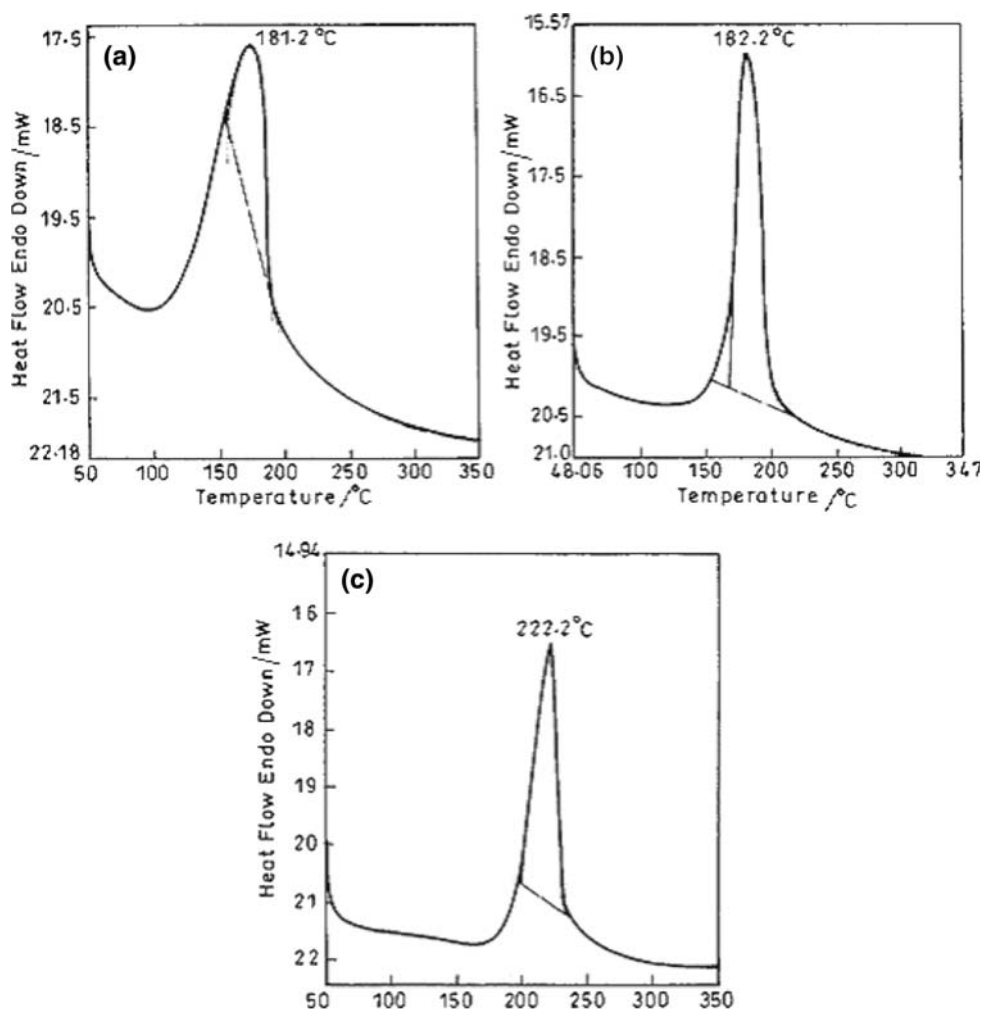


Table 5 Results of DSC scans of DGEBA/DIDAS

No.	Sample designation	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J g ⁻¹)
1	EPH	175.40	190.39	204.69	225.31	50.95
2	EOH	140.32	158.21	181.22	192.60	36.92
3	ENH	176.21	183.74	205.25	223.54	50.00
4	EPB	192.50	201.87	222.23	238.10	80.90
5	EOB	178.5	168.26	182.24	205.17	73.51
6	ENB	185.20	198.13	214.25	234.20	38.99

ΔH Heat of curing, calculated by measuring area under the exothermic.

Figure 4 shows DSC scans of DGEBA in the presence of stoichiometric amounts of DIDAS (a) OH, (b) OB, and (c) PB recorded at a heating rate of 10 °C/min, respectively. The results of DSC scans are summarized in Table 5. The curing temperature was depending upon the structure of dianhydride or amino carboxylic acids used in the preparation of DIDAS.

The curing mechanism of epoxy-imide acids involves reaction of acid functionality with the epoxy followed by esterification of the epoxy hydroxyl groups with the acids [24]. Onset temperature of exotherm (T_o) may be used as a criterion for evaluating the relative reactivity of various imino carboxylic acids. 4-Butyric acid based DIDAS show high curing temperatures than those based on 6-amino-hexanoic acid. This might be due to the steric hindrance in case of butyric acid (shorter chain), thus preventing the reaction of acid group as well as esterification of the epoxy

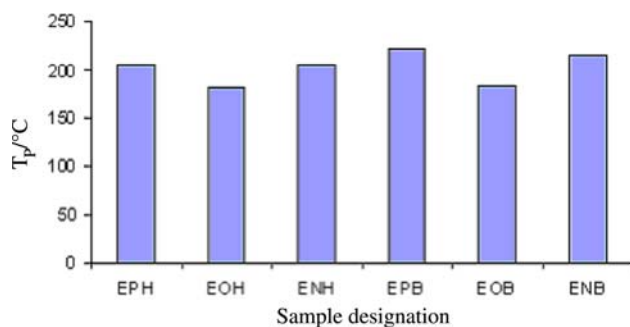


Fig. 5 Bar graph showing the trend in T_p value

hydroxyl groups with the acids. The lowest T_o was observed with the resin cured with OH/OB and the highest with the PH/PB. This data clearly shows that DIDAS based on ODA are more reactive than those based on PMDA. This could be due to the less stability of polynuclear compound. Comparing the DIDAS of varying structure, T_i , T_o , T_p and T_f were highest for the resin cured with EPB and lowest with EOH, but no definite trend was seen in T_p value as shown in Fig. 5. The lower ΔH value in case of DIDAS based on NTDA could be due to the non-accessibility of the curing agent for opening the epoxide ring because of the formation of rigid network structure.

Thermal behavior

The thermal stability of epoxy resin samples cured isothermally with a stoichiometric amount of DIDAS was determined by recording TG traces in nitrogen atmosphere. Figure 6 shows TG traces of epoxy resin samples, i.e.,

Fig. 6 TG traces of DGEBA cured isothermally with diimide-diacids: **a** PB, **b** NB and **c** OB

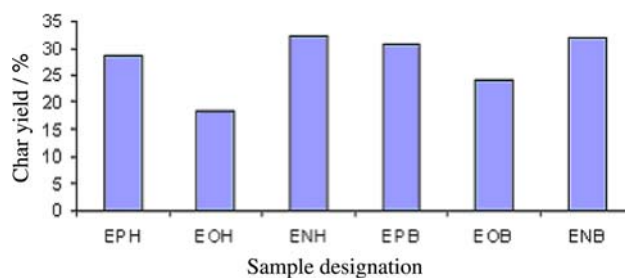
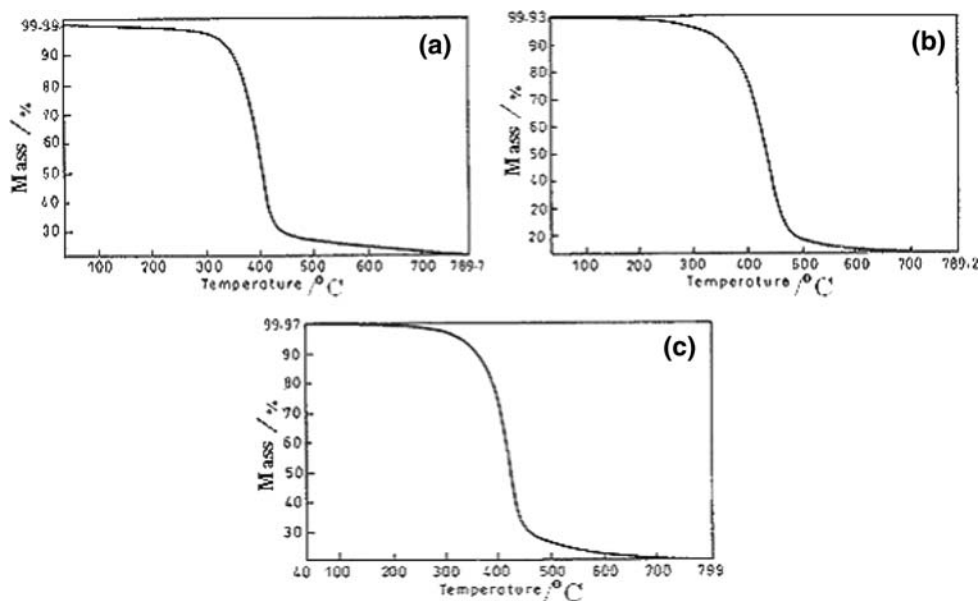


Fig. 7 Bar graph showing the trend in char yields value

ENB, EOB and EPB. The relative thermal stability of the cured resins was compared by noting initial decomposition temperature (IDT), final decomposition temperature (IDT), temperature of maximum rate of mass loss (T_{max}) and percent char yield at 800 °C. The results were summarized in Table 6. All the samples were stable upto 220 °C and a significant mass loss occurred only beyond this temperature. The char yield tends to dependent on the structure of DIDAS and it was highest for ENH and lowest for EOH. Figure 7 shows the trend in char yield values. Diimide-diacids based on NTDA gave resins with higher char yield as compared to those based on ODA. This can be explained on the basis of compact network structure present in naphthalene-based DIDAS. Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resin in accordance with Van Krevelen and Hoftzyer equation [25].

$$LOI = 17.5 + 0.4CR$$

where CR = char yield.

Table 6 Results of TG traces of DGEBA cured isothermally with DIDAS

No.	Sample designation	IDT (°C)	T_{\max} (°C)	FDT (°C)	Char yield at 800 °C (%)	LOI
1	EPH	258.00	432.21	516.32	28.77	29.00
2	EOH	237.11	439.14	530.01	18.30	24.82
3	ENH	256.48	420.71	512.72	32.14	30.35
4	EPB	221.54	418.64	473.92	30.61	29.74
5	EOB	243.25	425.18	538.00	24.18	27.17
6	ENB	232.43	404.36	495.17	31.98	30.29

All the samples had LOI values calculated based on their char yield was higher than 28 except for EOH/EOB. On the basis of LOI values, such materials can be classified as self-extinguishing resin and flame resistant DGEBA resin can be obtained by using DIDAS as curing agents.

Conclusions

The structure of synthesized DIDAS was confirmed through EA, FT-IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ characterization. The DIDAS based on ODA were more reactive than those based on PMDA. The curing temperature of exothermic transition depends on the structure of DIDAS. T_i , T_o , T_p and T_f were highest for the resin cured with EPB and lowest with EOH. Higher char yields were obtained with epoxy resins cured with DIDAS based on 'NTDA' as compared to 'ODA' or 'PMDA' based DIDAS. The highest char yield was observed in case of ENH/ENB and lowest with EOH/EOB.

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