

Interacting blends of novel acrylated poly(ester-amide) resins-III with methyl methacrylate monomer part-1

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ABSTRACT

Bisphthalamic acids were prepared by reaction of phthalic anhydride and aliphatic diamines. Novel poly(ester-amide) resins (PEAs) were prepared by reaction between diglycidyl ether of bisphenol-C (DGEBC) with bisphthalamic acids using a base catalyst like triethylamine (TEA). The post reactions of all these PEAs were carried out by using acryloyl chloride. The resultant products are designated as acrylated poly(ester-amide) resins (APEAs). The PEAs and APEAs were characterized by elemental analysis, number average molecular weight determined by non-aqueous conductometric titration method. IR spectra of PEAs were also recorded. Blending of these APEAs were carried out with methyl methacrylate monomer. The curing of these APEAs- methyl methacrylate monomer blends was monitored on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. Based on DSC data, the glass fiber reinforced composites of APEAs- methyl methacrylate monomer blends have been fabricated and their chemical, mechanical and electrical properties have been evaluated. The unreinforced cured samples of APEAs- methyl methacrylate monomer blends were analyzed thermogravimetrically (TGA).

Keywords: Diglycidyl ether of Bisphenol-C (DGEBC), Polyester, Polyamide, Number average molecular weight (\bar{M}_n), Differential scanning calorimeter (DSC), Thermogravimetric analysis (TGA), Interacting blends.

INTRODUCTION

Epoxy is also known as polyepoxide, and it is a thermosetting polymer formed from reaction of an epoxide resin with polyamine which is used as a hardener. Epoxy has a wide range of applications, including fiber-reinforced plastic materials and general purpose adhesives. The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiber glass reinforcements. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Many properties of epoxies can be modified [1, 2].

Polyester resins are used in sheet moulding compound, bulk moulding compound and it is well known that polyesters and polyamides are independent polymer candidates for a wide range of industrial application like composites, adhesive, anticorrosive coatings and others [3-5]. Merging of these three epoxy, ester and amide segments into one polymer chain may yield a polymer with better properties than these of the individual ones.

Hence recently some work in this direction has been carried out from our laboratory [6, 7]. In order to improve certain properties of such reported unsaturated polyester resins their blending with commercial vinyl ester epoxy resin is possible. While vinyl ester resin is versatile industrial resin and modification through blending is also possibility [8, 9]. Also thermoplastics modification via blending has been already reported from our laboratory [10-14]. Hence, the present article comprises the synthesis, characterization and glass fiber reinforcement of acrylated poly(ester-amide) resins with methyl methacrylate monomer. The synthesis step is scanned in Scheme 2.

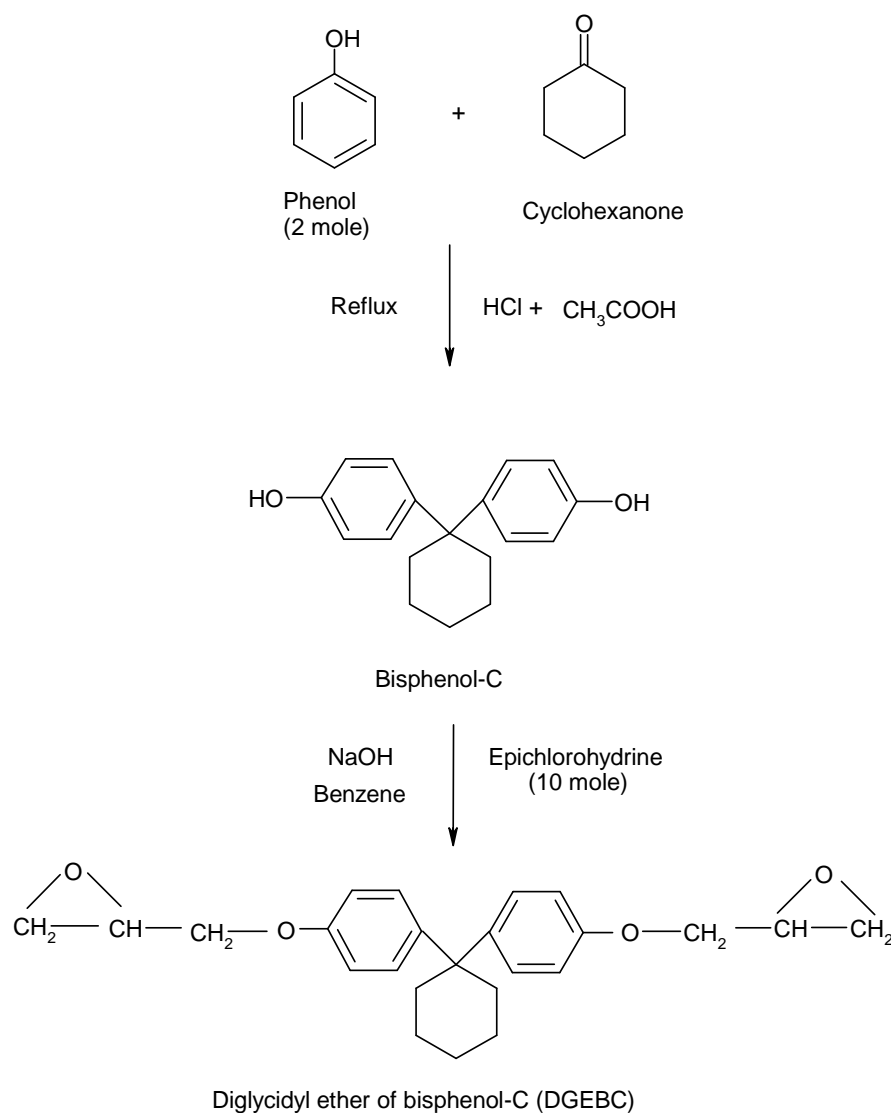
MATERIALS AND METHODS

Materials

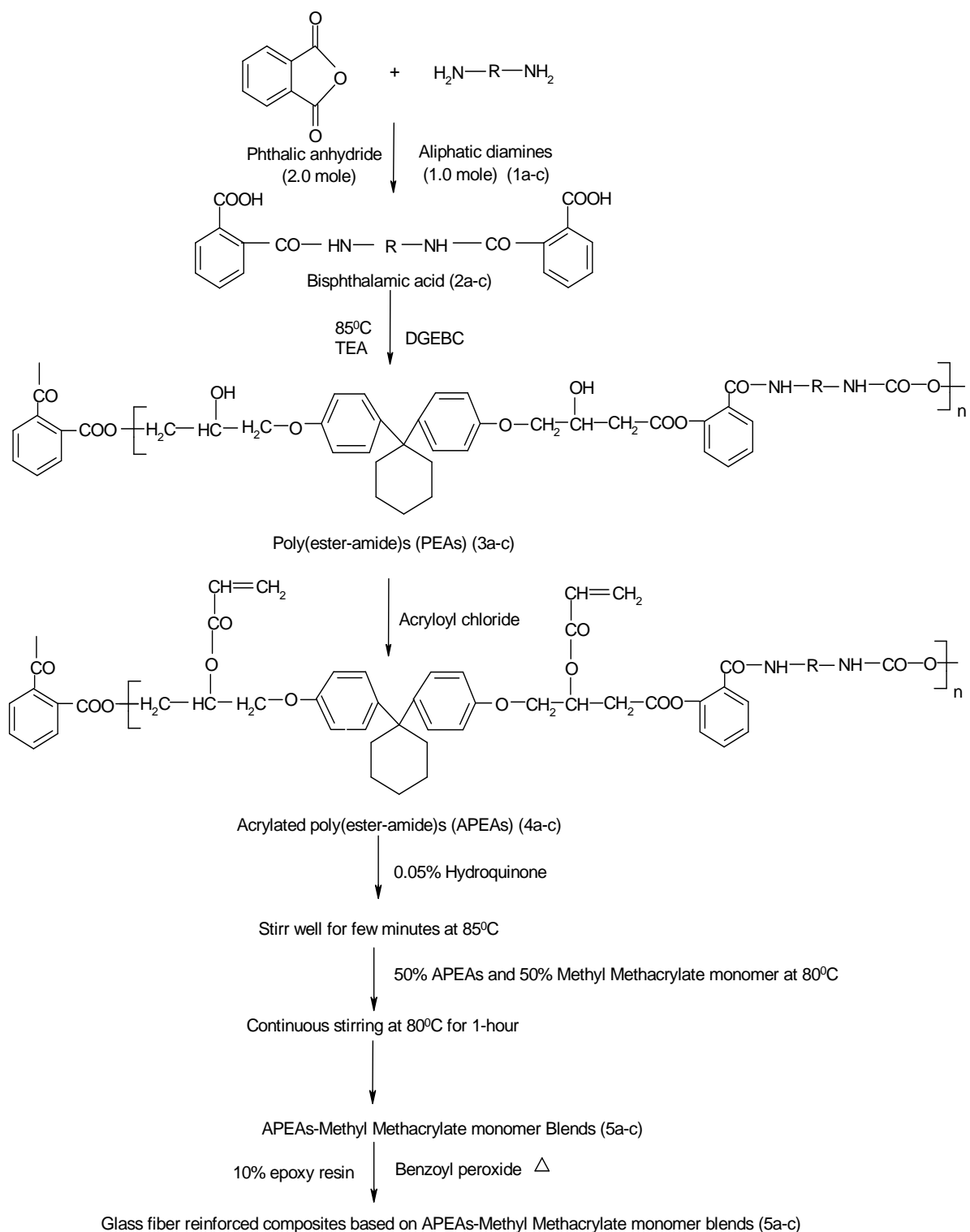
The aliphatic diamines used for the preparation bisphthalamic acids were,

1. 1,2-Ethane diamine,
2. 1,3-Propane diamine,
3. 1,6-Hexamethylene diamine.

E-type of glass woven fabric (poly (ester-amide) compatible) 0.25mm thick (Unnati Chemicals, India) of a real weight 270 g.m^{-2} were used for composite fabrication. All other chemicals used were of pure grade.



Scheme 1 Synthesis of DGEBC



Where, R = (1a) 1,2-Ethane diamine
 (1b) 1,3-Propane diamine
 (1c) 1,6-Hexamethylene diamine

Scheme 2 Synthesis steps for APEAs-Methyl Methacrylate monomer blends (5a-c)

Synthesis of Bisphenol-C

This was prepared according to the method described in literature [15]. The general procedure is as follows:

Cyclohexanone (49 gm, 0.5 mole) was treated with phenol (94 gm, 1 mole) in presence of a mixture of hydrochloric acid and acetic acid (150 ml 2:1 vol.) at 40°C for 5 hrs. and kept overnight at room temperature. A pink colored product was obtained which was separated out, by dissolving it in 2M NaOH solution. The mixture was then filtered to remove gummy product and then acidified to yield yellowish product. Product washed several times with benzene to remove any other impurities in the product. Recrystallization from methanol using charcoal gave a fine white product. The synthesis step for Bisphenol-C is scanned in Scheme 1.

Synthesis of diglycidyl ether of bisphenol-C (DGEBC)

Bisphenol-C (1 mole) was dissolved in the mixture of epichlorohydrin (10 mole) and water in a three necked flask. A reflux condenser was then attached to the flask and the mixture was heated until the epichlorohydrin begin to reflux heating was stopped and 2 mole of NaOH pellets were added in portions of two pellets at a time down the condenser. After the addition of one portion again the content of the flask was mixed by careful shaking and then carefully warmed again after the addition of a few portions of the sodium hydroxide and exothermic reaction begins. This is allowed to subside before further portions of sodium hydroxide are added. A bowl of cold water was made available so that the exothermic reaction may be moderated by cooling if necessary.

Then after careful addition of further NaOH, the reaction mixture was heated for 45 minutes. The mixture was then vacuum distilled in order to remove excess epichlorohydrin. After it benzene was added to give resin solution and to precipitate the sodium chloride formed during the reaction. The sodium chloride is filtered off. The filtered mixture returned to round bottom flask and vacuum distilled to recover benzene solvent. The synthesis step for diglycidyl ether of bisphenol-C (DGEBC) is scanned in Scheme 1.

Synthesis of Bisphthalamic Acids

The bisphthalamic acids were prepared by method reported in literature [7]. The general procedure is as follows:

To a well stirred solution of phthalic anhydride (2.0 mole) in dry acetone, the solution of aliphatic diamines (1a-c) (1.0 mole) in dry acetone was gradually added at room temperature within 30-minutes. After complete addition of the diamine solution the reaction mixture was further stirred for half an hour at room temperature. The resulting bisphthalamic acids were then treated washed with dry acetone and air dried. All the bisphthalamic acids (2a-c) were obtained in the form of free flowing powder. The synthesis step is scanned in scheme 2.

Synthesis of (PEAs) and (APEAs)

Epoxy resin (DGEBC) (1.0 mole) and bisphthalamic acids (2a-c) (1.0 mole) were charged in three necked flask equipped with a mechanical stirrer by following method re-reported for epoxy resin and carboxylic group [16]. To this 8.0% of the total weight of above, triethylamine (TEA) was added as a base catalyst. The reaction mixture was slowly heated up to 85 °C with continuous stirring. The reaction was continued till the acid value fell below 60 mg KOH/gm. The resultant resins were then discharged and are designated poly(ester-amide)s, PEAs (3a-c) and their details are furnished in Table 1. Further reaction of all these PEAs was carried out with acryloyl chloride (i.e. acrylation) and resultant products are called acrylated poly(ester-amide)s, designated as APEAs (4a-c) and their details are furnished in Table 2. The synthesis step is scanned in scheme 2.

Synthesis of APEAs- Methyl Methacrylate Blends (5a-c)

When the acid value of APEAs resins (4a-c) fell below 60 mg KOH/gm, 0.05% of hydroquinone was added as an inhibitor. The whole reaction stirred well for few minutes maintaining the temperature at 85°C then the temperature was lowered to 80°C and 50% of APEAs and 50% of methyl methacrylate monomer was added. The reaction mixture was then continuously stirred at 80°C for one hour. It is then discharged; all the blends obtained were in the form of viscous syrup designated as APEAs- methyl methacrylate monomer blends (5a-c). The synthetic steps are shown in Scheme 2.

Composite Fabrication

The composites were prepared by using E-type of glass fiber. The glass fiber: resin ratio is 60:40 (30% APEAs resin + 10% DGEBC). Suspensions of APEAs (4a-c) were prepared in tetrahydrofuran. In the suspension of above polymer 1% of ethylene dimethylacrylate (as a cross linking agent) with 0.05% benzoyl peroxide (as an initiator) were added and mixed well. The mixture was applied with a brush to a 200mm × 200mm glass cloth and the solvent was allowed to evaporate. The ten dried prepregs prepared in this way were then stacked one on top of another and pressed between steel plates coated with a "Teflon" film release sheet and compressed under 70 psi pressure. The prepregs stacks were cured by heating it in an autoclave oven at 220°C for about 6 hour. The composites so obtained were cooled to 45-50°C before the pressure was released. The composites were then machined to final dimensions.

MEASUREMENTS

Elemental Analysis

The C, H, and N content of all the PEAs (3a-c) and APEAs (4a-c) were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). The number average molecular weight of all the PEAs (3a-c) and APEAs (4a-c) were estimated by non-aqueous conductometric titration following method reported in an earlier communication [17]. The IR spectra were recorded in Kerr pellets on a Nicollet 760 D spectrometer for both PEAs (3a-c) and APEAs (4a-c). Number of hydroxyl groups present per repeating unit in PEAs (3a-c) was analyzed by employing acetylating method [18]. Also, APEAs (4a-c) were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method [19]. All the results for number of -OH group for PEAs (3a-c) and presence of double bonds for APEAs (4a-c) are found to be consistent with the predicted structures and the results are furnished in Table 1 and 2 respectively.

Curing

Curing of all these APEAs- methyl methacrylate monomer blends (5a-c) were carried out on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. A Du-Pont 900 DSC was used for this study. The instrument was calibrated using standard indium metal with known heat of fusion ($\Delta H=28.45\text{J/g}$). Curing was carried out from 30-300°C at 10°C min⁻¹ heating rate. The sample weight used for this investigation was in the range of 4-5 mg along with an empty reference cell. The results are furnished in Table 3.

Unreinforced cured samples of APEAs- methyl methacrylate monomer blends (5a-c) were subjected to thermogravimetric analysis (TGA) on Du-Pont 950 thermo gravimetric analyzer in air at a heating rate of 10°C min⁻¹. The sample weight used for this investigation was in the range of 4-5 mg. The results are furnished in Table 4.

CHARACTERIZATIONS OF COMPOSITE SAMPLES

All the chemical, mechanical and electrical tests on composites were conducted according to ASTM methods (as listed below) using three specimens for each test.

Chemical Resistance Test

The resistances against chemicals of the composite samples were measured according to ASTM D 543. The chemicals used for the study were H₂SO₄ (25% v/v), HCl (25% v/v), NaOH (25% w/v), ethanol, acetone, DMF and THF. The tests were performed by dipping the composite samples in 100ml each of the reagents for 7 days at room temperature. After 7 days the specimens were taken out from the reagents and after drying they were examined for the percentage changes in thickness and weight. The results are furnished in Table 5.

Mechanical and Electrical Testing

- (1) The Flexural strength was measured according to ASTM D 790.
- (2) The Compressive strength was measured according to ASTM D 695.
- (3) The Impact strength was measured according to ASTM D 256.
- (4) The Rockwell hardness was measured according to ASTM D 785.
- (5) The Electrical strength was measured according to ASTM D 149.

The results are furnished in Table 6.

All mechanical and electrical tests were performed using three specimens and their average results were considered.

RESULTS AND DISCUSSION

Novel poly(ester-amide)s (PEAs) (3a-c) was prepared by reaction of epoxy resin (DGEBC) with bisphthalamic acids using a base catalyst. The post reactions of all these PEAs were carried out with acryloyl chloride. The resultant products are designated as acrylated poly(ester-amide)s (APEAs) (4a-c). The APEAs- methyl methacrylate monomer blends were prepared by method described as above.

The C, H and N content of all the PEAs (3a-c) and APEAs (4a-c) were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). Their results are furnished in Table 1 and 2 respectively. From the results we can say that values of C, H and N content of each PEAs (3a-c) and APEAs (4a-c) were consistent with their predicted structures. The number average molecular weight of all the PEAs (3a-c) and APEAs (4a-c) were estimated by non-aqueous conductometric titration following by method [17]. Their results are furnished in Table 1 and 2 respectively.

The IR spectra were recorded in Kerr pellets on a Nicollet 760 D spectrometer for both PEAs (3a-c). The IR spectra of all PEAs (3a-c) were consistent with their predicted structures. The IR spectra of all PEAs resin show the

prominent position of important segments in the polymer chain. The broad band from 3600-2500 cm^{-1} with inflexions at 2850-2920 cm^{-1} this broad band mainly due to secondary –OH groups. This is supported by the strong band at 1100 cm^{-1} . The inflexions are raised from –CH₂ groups present in epoxy resin and aliphatic diamines. The bands due to presence of aliphatic segments are at their expected position. The only discernible difference between spectra of epoxy resin and PEAs resins reveals that the band at 910 cm^{-1} appeared in the spectrum of epoxy groups is almost vanished in the spectra of PEAs resins and a new band appear at 1680 cm^{-1} from ester group. This confirms the reaction between DGEBC and bisphthalamic acids. The IR spectra of PEAs resins are given in Table 1 and the IR spectra of sample (3a) is shown in Figure 1.

TABLE 1 Characterization of PEAs (3a-c)

PEAs (3a-c)	Elemental analysis (Wt %)			No. of –OH group per repeating unit	Number average molecular weight (\bar{M}_n) \pm 60
	Calc. / (Found)				
	%C	%H	%N		
3a	66.45 (66.30)	6.32 (6.10)	4.43 (4.21)	1.94	3748
3b	66.87 (66.69)	6.50 (6.33)	4.33 (4.12)	1.91	3827
3c	68.02 (67.74)	6.97 (6.81)	4.06 (3.84)	1.91	4070

TABLE 2 Characterization of APEAs (4a-c)

APEAs (4a-c)	Elemental analysis (Wt %)			No. of double bonds per repeating unit	Number average molecular weight (\bar{M}_n) \pm 60
	Calc. / (Found)				
	%C	%H	%N		
4a	67.95 (67.71)	6.07 (5.91)	3.86 (3.75)	1.92	4306
4b	68.29 (68.04)	6.23 (6.11)	3.79 (3.63)	1.92	4384
4c	69.23 (69.08)	6.66 (6.54)	3.58 (3.42)	1.94	4627

TABLE 3 DSC curing of APEAs- Methyl Methacrylate monomer blends (5a-c)

APEAs-MMA monomer blends (5a-c)	Curing Temperature ($^{\circ}\text{C}$)		
	Ti	Tp	Tf
5a	131	145	166
5b	130	148	159
5c	138	160	187

TABLE 4 TGA of Unreinforced cured samples of APEAs- Methyl Methacrylate monomer blends (5a-c)

APEAs-MMA monomer blends (5a-c)	% Weight loss at various temps. ($^{\circ}\text{C}$) from TGA				
	150 $^{\circ}\text{C}$	300 $^{\circ}\text{C}$	450 $^{\circ}\text{C}$	600 $^{\circ}\text{C}$	750 $^{\circ}\text{C}$
5a	3.98	13.78	56.31	80.13	87.43
5b	3.91	13.74	56.27	80.41	87.13
5c	3.80	13.60	54.61	80.33	87.22

TABLE 5 Chemical resistance properties of APEAs- Methyl Methacrylate monomer blends (5a-c)

Reagents	% Change in APEAs- MMA monomer blends (5a-c)					
	5a		5b		5c	
	Thickness	Weight	Thickness	Weight	Thickness	Weight
H ₂ SO ₄	1.06	1.76	1.11	1.80	1.12	1.83
HCl	0.81	1.19	0.86	1.22	0.21	1.25
NaOH	0.75	1.09	0.73	1.12	0.80	1.17
Ethanol	0.22	0.33	0.25	0.35	0.25	0.36
Acetone	0.21	0.26	0.22	0.30	0.27	0.35
DMF	1.10	1.80	0.17	1.87	0.18	1.90
THF	0.55	0.72	0.56	0.76	0.62	0.79

TABLE 6 Mechanical and Electrical properties of APEAs- Methyl Methacrylate monomer blends (5a-c)

Composites of APEAs- MMA monomer blends (5a-c)	Flexural Strength (MPa)	Impact Strength (MPa)	Compressive Strength (MPa)	Rockwell Hardness (R)	Electrical Strength in air (kV/mm)
5a	389	412	400	91	21.12
5b	395	418	407	97	21.15
5c	402	421	411	103	21.17

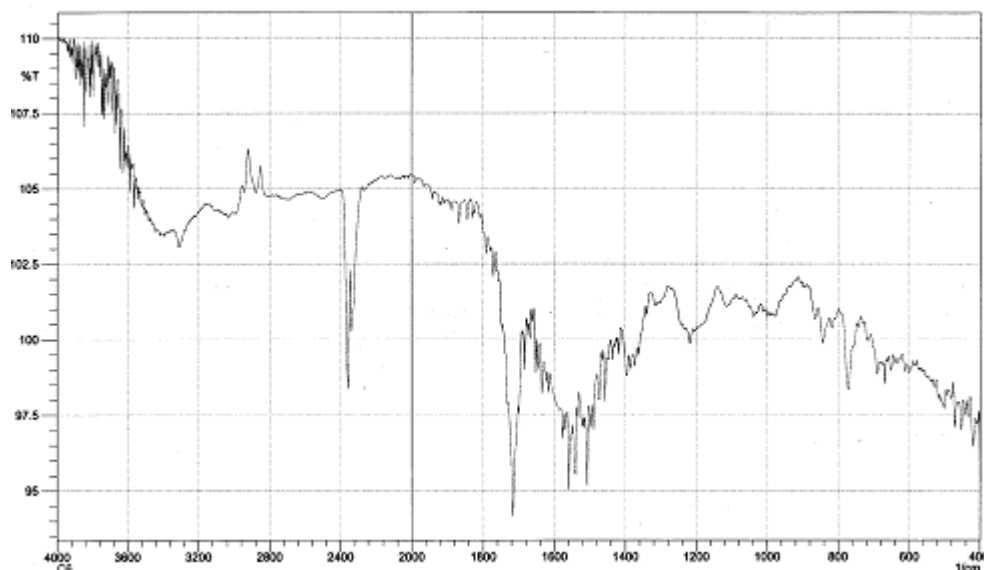


Figure 1 IR spectra of sample (3a)

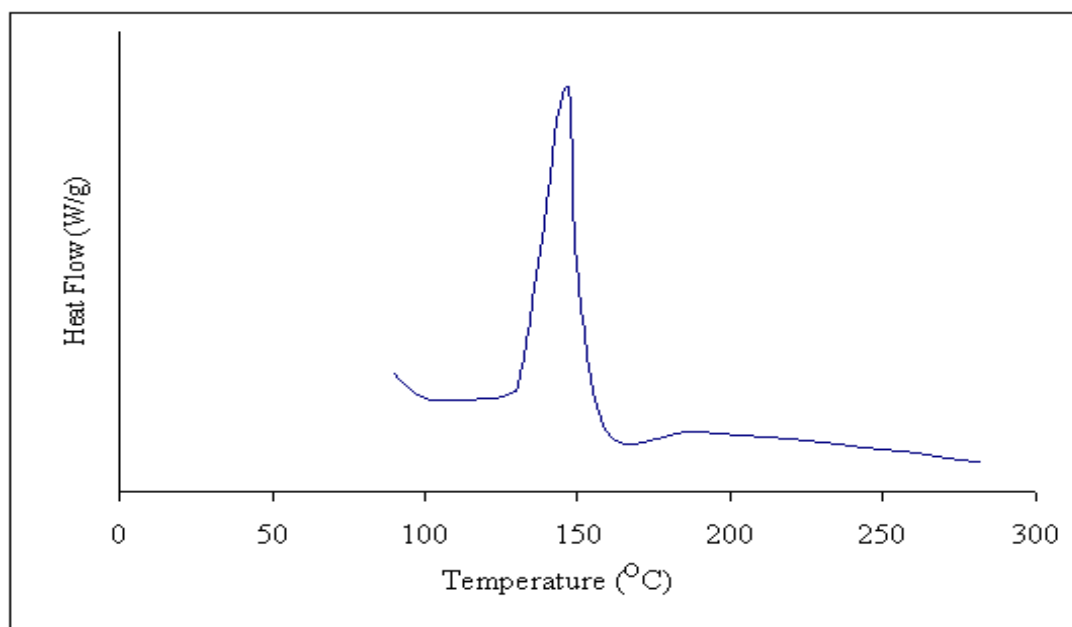


Figure 2 DSC of sample (5b)

Number of hydroxyl groups present per repeating unit in PEAs (3a-c) was also analyzed by employing acetylating method [18]. Also, APEAs (4a-c) were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method [19]. Satisfactory results were found and the results are furnished in Table 1 and 2 respectively.

Curing of all these APEAs- methyl methacrylate monomer blends (5a-c) were carried out on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. A Du Pont 900 DSC was used for this study. The data of DSC thermograms of all APEAs- methyl methacrylate monomer blends (5a-c) are furnished in Table 3 and DSC of sample (5c) is shown in Figure 2.

The unreinforced cured samples of APEAs- methyl methacrylate monomer blends (5a-c) were also analyzed by thermo gravimetric analysis (TGA). The result reveals that the cured sample starts their degradation at about 150°C and their initial weight is about 2%. This small weight loss may be due to either in sufficient curing of components used or due to the catalyst used. A weight loss of about 14% is found at 300°C. However, the rate of decomposition increases very rapidly between 300°C to 450°C and reach up to 56% and the products are lost completely beyond

750°C. TGA data of all the cured samples are shown in Table 4 and TG thermogram of sample (5a) is shown in Figure 3

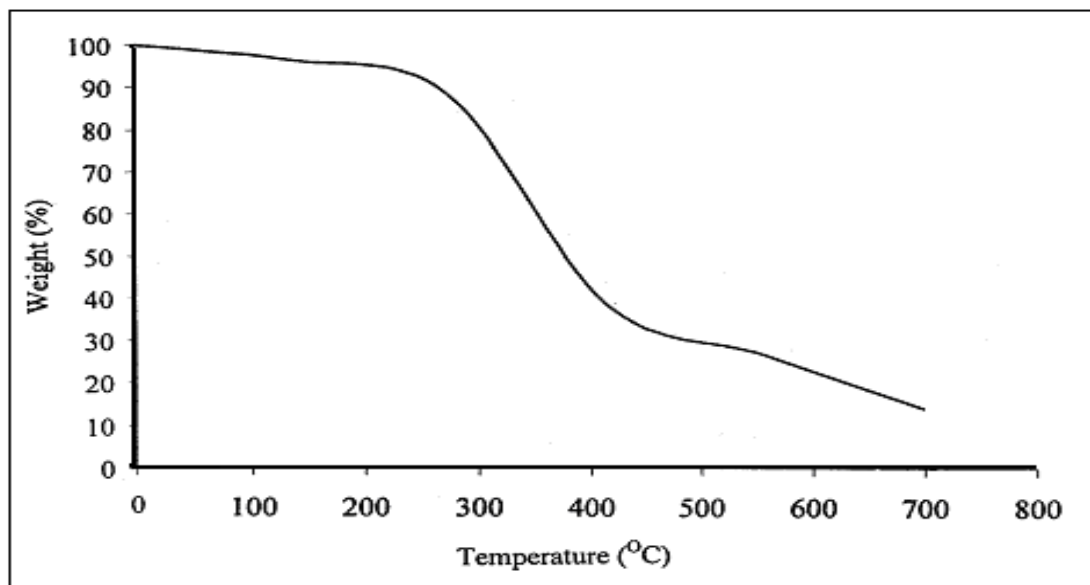


Figure 3 TG Thermogram of sample (5a)

The Glass fiber reinforced composites of all APEAs- methyl methacrylate monomer blends (5a-c) were prepared based on their DSC data. The composites were characterized for their chemical resistance test their results are furnished in Table 5. The composites were also characterized for their mechanical and electrical tests. Their results are furnished in Table 6. The results shows that composites have good chemical resistant property, good mechanical and electrical strength.

CONCLUSION

From the characterizations of APEAs- methyl methacrylate monomer blends the following conclusions have been made.

Rather than using novel APEAs the blends of APEAs- methyl methacrylate monomer blends is more advantageous. The results furnished in Table 3 to 6 itself suggests that these blends give high curing temperature, slow degradation of product (i.e. low weight loss), good chemical resistance, good mechanical and good electrical strength. The results show that blends of APEAs- methyl methacrylate monomer can be competitor to commercial polyester resins.

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