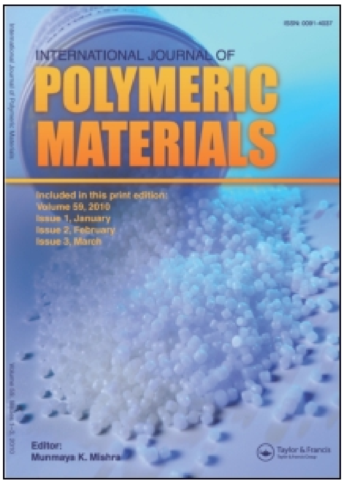

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Interacting Blends of Novel Acrylated Poly(Ester Amide)s Based on DGEBC with Styrene Monomer

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

Keywords: differential scanning calorimeter (DSC), epoxy resin (DGEBC), interacting blends, number average molecular weight ($\overline{Mn}$), polyamide, polyester, thermogravimetric analysis (TGA)

INTRODUCTION

It is well-known that epoxy resins, polyesters and polyamides are independent polymer candidates for a wide range of industrial applications such as composites, adhesive, anticorrosive coatings and others

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[1–5]. Merging of these three epoxy, ester and amide segments into one polymer chain may yield a polymer with better properties than the individual ones.

Hence, recently, work in this direction has been carried out in our laboratory [6,7]. In continuation of this work, the interacting blends of poly(ester amide)s with vinyl monomers has also been reported from our laboratory [8]. The present article comprises the study of APEAs-styrene blends.

EXPERIMENTAL

Materials

The diamines used for bisphthalamic acids were:

(1a) 1,4-phenylene diamine,
(1b) 4,4′-diamno diphenyl methane,
(1c) 4,4′-diamino diphenyl sulfone.

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

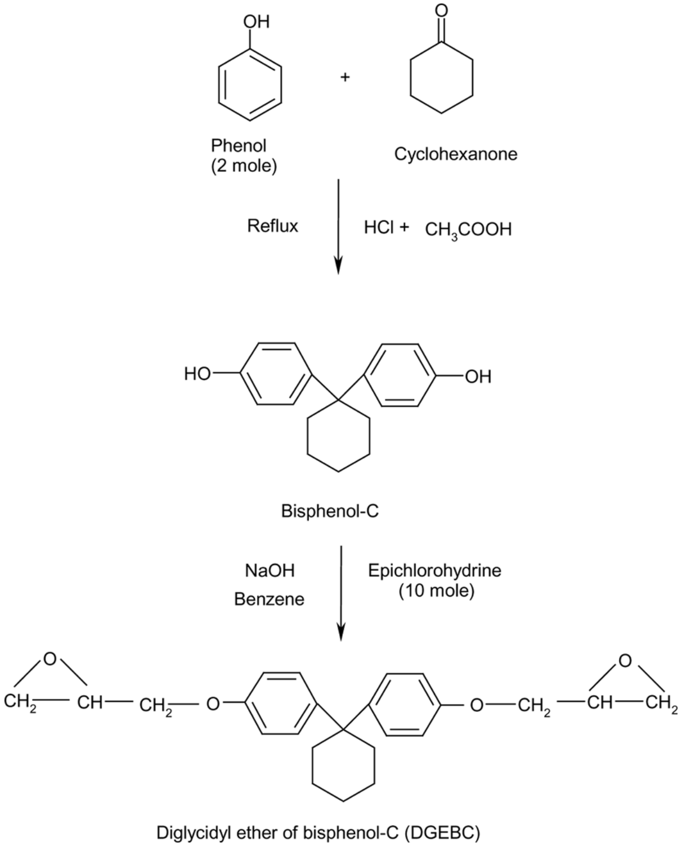
Synthesis of Bisphenol-C

This was prepared according to the method described in the literature [9]. The general procedure is as follows:

Cyclohexanone (49 gm, 0.5 mol) was treated with phenol (94 g, 1 mol) in the presence of a mixture of hydrochloric acid and acetic acid (150 ml 2:1 vol.) at 40°C for 5 h. and kept overnight at room temperature. A pink-colored product was obtained which was separated out by dissolving it in 2 M NaOH solution. The mixture was then filtered to remove gummy product and then acidified to yield yellowish product. The product was washed several times with benzene to remove any other impurities. 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)

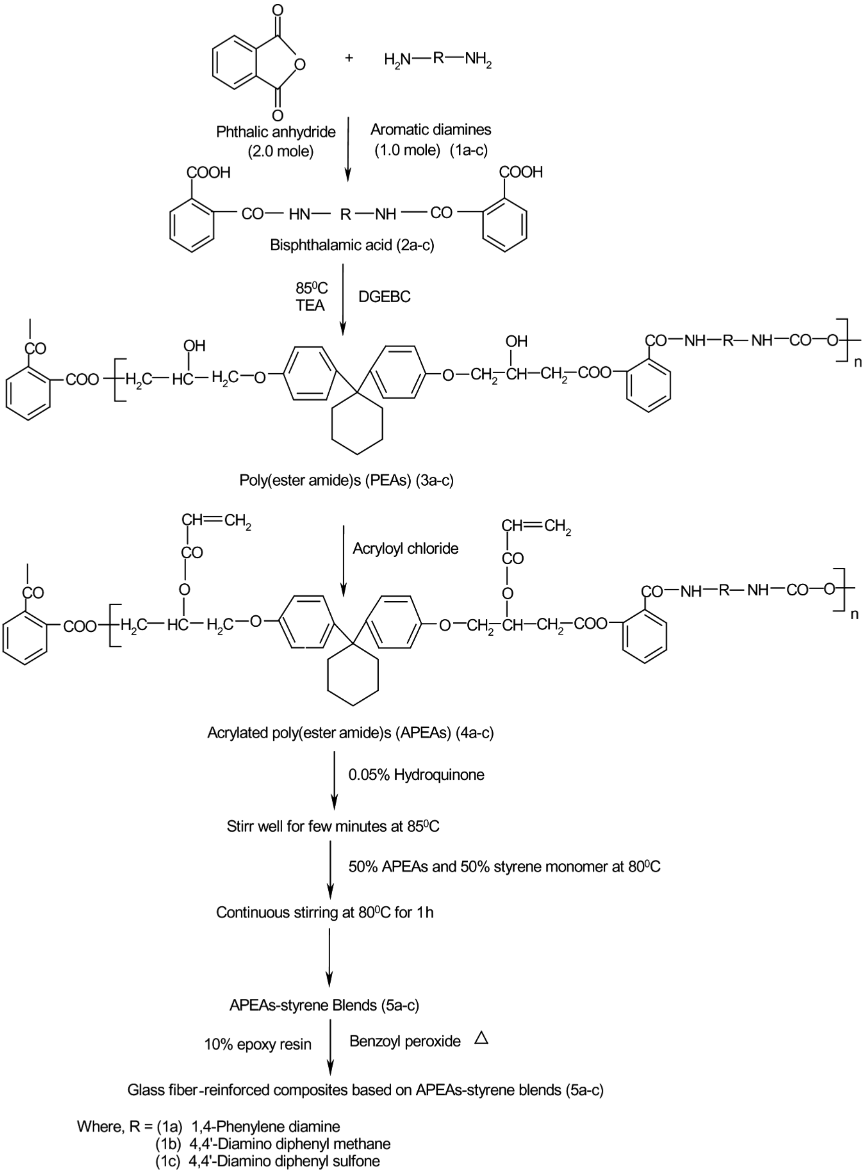
Bisphenol-C (1 mol) was dissolved in a mixture of epichlorohydrin (10 mol) and water in a three-necked flask. A reflux condenser was then attached to the flask and the mixture was heated until the epichlorohydrin began to reflux. Heating was stopped and 2 mol of NaOH



SCHEME 1 Synthesis of DGEBC.

pellets were added in portions of two pellets at a time down the condenser. After the addition of each portion, 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 an exothermic reaction began. This was allowed to subside before further portions of sodium hydroxide were 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 min. The mixture was then vacuum-distilled in order to remove excess epichlorohydrin. Benzene was then added to give resin solution and to precipitate the sodium chloride formed during the reaction. The sodium chloride was filtered off. The filtered mixture was returned to a round-bottom flask and vacuum-distilled to recover benzene solvent. The synthesis step for diglycidyl ether of bisphenol-C (DGEBC) is shown in Scheme 1.



SCHEME 2 Synthesis steps for APEAs-styrene monomer blends (5a-c).

Synthesis of Bisphthalamic Acids

The bisphthalamic acids were prepared by the method reported in the literature [10]. The general procedure is as follows:

To each well-stirred solution of phthalic anhydride (2.0 mol) in dry acetone, a separate solution of aromatic diamine (1a-c) (1.0 mol) in dry acetone was gradually added at room temperature within 30 min. After complete addition of the diamine solution, the reaction mixture was stirred for further half an hour at room temperature. The resulting bisphthalamic acids were then 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)

The bisphthalamic acids (2a-c) were then treated with epoxy resin (DGEBC). Epoxy resin (DGEBC) (1.0 mol) and bisphthalamic acids (2a-c) (1.0 mol) were charged in a three-necked flask equipped with a mechanical stirrer. To this, 8.0% of the total weight of above triethylamine (TEA) was added as a base catalyst. The reaction mixture was slowly heated 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 these PEAs was carried out with acryloyl chloride (i.e., acrylation) and the resultant products, called acrylated poly(ester amide)s and designated as APEAs (4a-c), are detailed in Table 2. The synthesis step is scanned in Scheme 2.

Synthesis of APEAs-Styrene 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 was stirred well for a few minutes while maintaining

TABLE 1 Characterization of PEAs (3a-c)

PEAs	Elemental analysis (wt%) Calc./(Found)				No. of –OH group per repeating unit	Number average molecular weight $(\overline{Mn}) \pm 60$
	% C	% H	% N	% S		
3a	68.82 (68.72)	5.88 (5.78)	4.11 (4.03)	—	1.92	4037
3b	71.68 (71.61)	5.97 (5.89)	3.63 (3.57)	—	1.94	4651
3c	65.85 (65.77)	5.36 (5.24)	3.41 (3.33)	3.90 (3.78)	1.94	4864

TABLE 2 Characterization of APEAs (4a-c)

APEAs samples	Elemental analysis (wt %) Calc./(Found) % C	% H	% N	% S	No. of double bonds per repeating unit	Number average molecular weight ($\overline{Mn}$) ± 60
4a	68.52 (68.43)	5.58 (5.47)	3.55 (3.41)	—	1.93	4781
4b	70.98 (70.89)	5.68 (5.57)	3.18 (3.09)	—	1.94	5314
4c	65.94 (65.83)	5.17 (5.09)	3.01 (2.92)	3.44 (3.36)	1.93	5515

the temperature at 85°C. Then the temperature was lowered to 80°C and 50% of APEAs and 50% of styrene monomer were added. The reaction mixture was then continuously stirred at 80°C for one hour. It was then discharged. All the blends obtained were in the form of viscous syrup designated as APEAs-styrene blends (5a-c). The synthetic steps are shown in Scheme 2.

Composite Fabrication

The composites were prepared by using E-type glass fiber. The glass fiber: resin ratio is 60:40 (30% APEAs resin + 10% DGEBC). Suspensions of APEAs (4a-c) were prepared in tetrahydrofuran. To the suspension of the above polymer, 1% of ethylene dimethylacrylate (as a crosslinking agent) with 0.05% benzoyl peroxide (as an initiator) were added and mixed well. The mixture was applied with a brush to a 200 mm × 200 mm 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 release sheet and compressed under 70 psi pressure. The prepreg stacks were cured by heating in an autoclave oven at 220°C for about 6 h. 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, N and S 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 nonaqueous conductometric titration following a method reported in an earlier

TABLE 3 DSC Curing of APEAs-Styrene Blends (5a-c)

APEAs-styrene blends	Curing temperature (°C)		
	Ti	Tp	Tf
5a	107	134	153
5b	111	138	160
5c	114	144	167

communication [11]. The IR spectra were recorded in Kerr pellets on a Nicollet 760 D spectrometer for both PEAs (3a-c) and APEAs (4a-c). The number of hydroxyl groups present per repeating unit in PEAs (3a-c) was analyzed by employing the acetylating method [12]. Also, APEAs (4a-c) were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method [13]. All the results for the number of –OH group for PEAs (3a-c) and presence of double bonds for APEAs (4a-c) were found to be consistent with the predicted structures and the results are furnished in Tables 1 and 2, respectively.

Curing

Curing of all the APEAs-styrene 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 ($\Delta H = 28.45\,J/g$). Curing was carried out from 30–300°C at $10^{\circ}C\,min^{-1}$ 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-styrene blends (5a-c) were subjected to thermogravimetric analysis (TGA) on Du-Pont 950 thermogravimetric analyzer in air at a heating rate of $10^{\circ}C\ min^{-1}$.

TABLE 4 TGA of Unreinforced Cured Samples of APEAs-Styrene Blends (5a-c)

APEAs-styrene blends	% Weight loss at various temps. (°C) from TGA				
	150°C	300°C	450°C	600°C	750°C
5a	1.82	9.81	61.09	76.52	80.25
5b	1.59	9.60	59.51	75.27	79.96
5c	1.40	9.56	56.79	71.08	78.63

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 H_2SO_4 (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 100 ml 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 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.

TABLE 5 Chemical Resistance Properties of APEAs-Styrene Blends (5a-c)

	% Change in APEAs-styrene blends (5a-c)					
	5a		5b		5c	
Reagents	Thickness	Weight	Thickness	Weight	Thickness	Weight
H_2SO_4	1.08	1.80	1.10	1.81	1.13	1.84
HCl	0.83	1.20	0.85	1.21	0.20	1.27
NaOH	0.72	1.08	0.75	1.11	0.78	1.16
Ethanol	0.21	0.31	0.23	0.34	0.26	0.38
Acetone	0.20	0.29	0.21	0.32	0.25	0.33
DMF	1.09	1.84	0.16	1.89	0.15	1.91
THF	0.52	0.73	0.57	0.78	0.61	0.80

TABLE 6 Mechanical and Electrical Properties of APEAs-Styrene Blends (5a-c)

Composites of APEAs-styrene blends (5a-c)	Flexural strength (MPa)	Impact strength (MPa)	Compressive strength (MPa)	Rockwell hardness (R)	Electrical strength in air (kV/mm)
5a	391	409	399	83	21.2
5b	394	411	395	83	21.5
5c	398	414	391	85	21.7

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. 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-styrene blends were prepared by the method described above.

The C, H, N and S 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 Tables 1 and 2, respectively. From the results we can say that values of C, H, N and S 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 nonaqueous conductometric titration following by method [11]. Their results are furnished in Tables 1 and 2, respectively. The IR spectra were recorded in Kerr pellets on a Nicollet 760 D spectrometer for both PEAs (3a-c) and APEAs (4a-c). The IR spectra of all PEAs (3a-c) and APEAs (4a-c) were consistent with their predicted structures.

Number of hydroxyl groups present per repeating unit in PEAs (3a-c) was determined by employing acetylating method [12]. Also, APEAs (4a-c) were characterized for the presence of double bonds per repeat unit, employing the mercury-catalyzed bromate-bromide method [13]. Satisfactory results were found and the results are furnished in Tables 1 and 2, respectively.

Curing of all these APEAs-styrene blends (5a-c) was 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-styrene blends (5a-c) are furnished in Table 3.

The unreinforced cured samples of APEAs-styrene blends (5a-c) were also analyzed by thermogravimetric analysis (TGA). The result reveals that the cured sample starts its degradation at about 150°C and the initial weight loss is about 2%. This small weight loss may be due to either insufficient curing of components used or due to the catalyst used. A weight loss of about 10% is found at 300°C. However, the rate of decomposition increases very rapidly between 300 to 450°C and up to 61% of the products are lost completely at 750°C. TGA data of all the cured samples are shown in Table 4.

The glass fiber-reinforced composites of all APEAs-styrene blends (5a-c) were prepared based on their DSC data. The composites were characterized for their chemical resistance test; the 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 show that the composites have good chemical resistance and good mechanical and electrical strengths.

CONCLUSIONS

From the characterizations of APEAs-styrene blends the following conclusions have been made.

Rather than using novel APEAs the blends of APEAs-styrene are more advantageous. The results furnished in Tables 3 to 6 suggest 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-styrene monomer can be a competitor to commercial polyester resins.

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