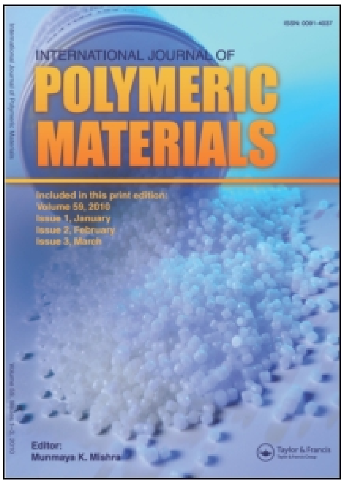

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Interacting Blends of Novel Acrylated Poly(Ester-Amide)s Based on Epoxy Resin of Bisphenol-F with Methyl Methacrylate Monomer

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Bisphthalamic acids were prepared by reaction of phthalic anhydride and aromatic diamines. Novel poly(ester-amide)s (PEAs) were prepared by reaction between epoxy resin of bisphenol-F and bisphthalamic acids. The post reactions of all these PEAs were carried out with acryloyl chloride. The resultant products are called acrylated poly(ester-amide)s (APEAs). Both PEAs and APEAs were characterized by IR spectral studies, elemental analysis and number average molecular weight ($\overline{Mn}$) determined by nonaqueous conductometric titration. Blending of these APEAs were carried out with methyl methacrylate monomer (APEAs-MMA blends). The curing of APEAs-MMA blends was monitored on a differential scanning calorimeter (DSC) and their kinetic parameters have been also evaluated. Based on DSC data, glass and carbon fiber-reinforced composites of APEAs-MMA blends have been fabricated and their chemical, mechanical and electrical properties have been evaluated. The unreinforced cured samples of APEAs-MMA blends were analyzed thermogravimetrically.

Keywords carbon fiber-reinforced composite (CFRC), differential scanning calorimeter (DSC), epoxy resin (DGEBF), glass fiber-reinforced composite (GFRC), interacting blends, number average molecular weight ($\overline{Mn}$), thermogravimetric analysis (TGA)

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INTRODUCTION

The epoxy resins are used in a large number of products, including surface coatings, adhesives, and reinforcing with carbon fiber [1,2]. The polyesters are the most widely versatile materials and have a broad spectrum of characteristics and wide applications ranging from aerospace to micro-electronics. They are also important as laminating resins, molding composites, fibers, films, surface-coating resins, and fiber cushions [3,4]. Polyamides are used in the form of fibers and other engineering applications. The glass fiber-reinforced nylon plastics are now of substantial importance due to rigidity and creep resistance. Polyamides are also used in automotive industries, and for valve covers and coatings [5,6].

Merging all three epoxy, ester and amide segments into one polymer chain has not received attention academically and technically, but has been recently reported from our laboratory [7–9]. Certain properties of thermoplastics may be improved via blending or by addition to a thermoset. In order to improve certain properties, the blending of unsaturated polyester amide resin has been also reported from our laboratory [10,11].

In extension of these works, the present communication comprises interacting blends of acrylated poly(ester-amide)s based on epoxy resin of bisphenol-F with methyl methacrylate monomer. Also, glass and carbon fiber-reinforced composites of these blends have been laminated and characterized by chemical, mechanical and electrical properties. The synthetic steps are shown in Scheme 1.

EXPERIMENTAL AND RESULTS

Materials

Commercially available diglycidylether of bisphenol-F (DGEBF) was obtained from Atul Ltd. Its epoxy equivalent weight is 160.

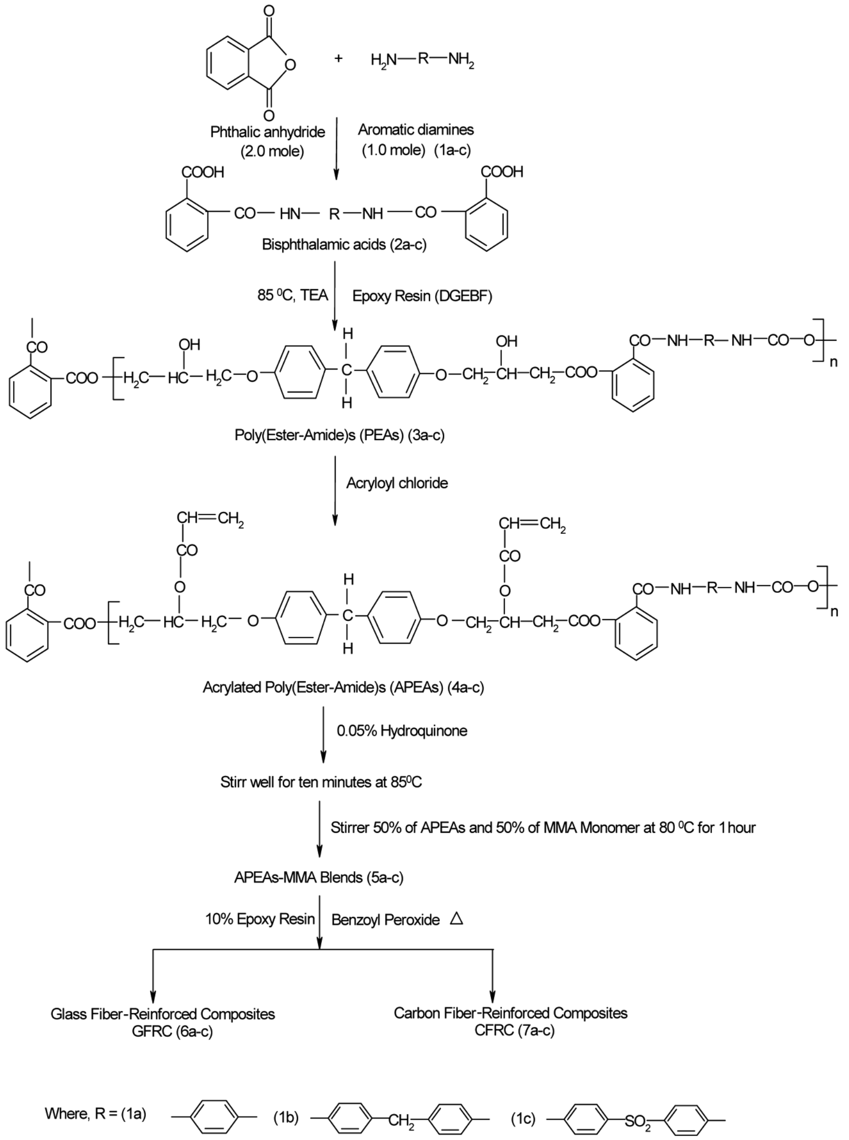
The diamines used for bisphthalamic acids were

(1a) 1,4-phenylene diamine

(1b) 4,4′-diamno diphenyl methane, and

(1c) 4,4′-diamino diphenyl sulfone.

E-type glass-woven fabric (0.25 mm thick) was obtained from Unnati Chemicals, India, and used for glass fiber reinforcement. Carbon fiber (12 K) was obtained from Reliance, IPCL, Vadodara, India, and used for carbon fiber reinforcement. All other chemicals used were of pure grade.



Scheme 1: Synthesis steps.

Preparation of Bisphthalamic Acids

The bisphthalamic acids were prepared by a method reported in the literature [12]. The general procedure is as follows:

To a well-stirred solution of phthalic anhydride (2.0 mole) in dry acetone, each solution of aromatic diamines 1a–c (1.0 mole) in dry acetone was gradually added at room temperature within 30 min. After complete addition of the

Table 1: Characterization of PEAs (3a–c).

PEAs	Elemental analysis (Wt %) calc./(found) %C	%H	%N	%S	No. of –OH group per repeating unit	Number average molecular weight $(\overline{\mathrm{Mn}}) \pm 60$
3a	66.66 (66.49)	5.22 (5.11)	4.57 (4.39)	—	1.94	3730
3b	70.08 (69.91)	5.41 (5.29)	3.98 (3.87)	—	1.94	4239
3c	63.82 (63.69)	4.78 (4.56)	3.72 (3.59)	4.25 (4.04)	1.96	4464

diamine solution the reaction mixture was further stirred for a half-hour at room temperature. The resulting bisphthalamic acids were then filtered, washed with dry acetone, and air-dried. All the bisphthalamic acids (2a–c) were obtained in the form of free-flowing powder.

Preparation of Poly(Ester-Amide)s (3a–c) and Acrylated Poly(Ester-Amide)s (4a–c)

Epoxy resin (DGEBF) (1.0 mole) and bisphthalamic acids (2a–c) (1.0 mole) were mixed well by vigorous agitation by mechanical stirrer. A little diethyl ether was added as a solvent for good suspension. 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. Samples were taken at regular intervals to check the acid value. The reaction was continued till the acid value fell below 55 mg KOH/gm. The resultant products are called poly(ester-amide)s, PEAs (3a–c) and their details are furnished in Table 1. Further reaction of all of these PEAs (3a–c) was carried out with

Table 2: Characterizations of APEAs (4a–c).

APEAs	Elemental analysis (Wt %) calc./(found) %C	%H	%N	%S	No. of double bonds per repeating unit	Number average molecular weight $(\overline{\mathrm{Mn}}) \pm 60$
4a	66.66 (66.47)	5.00 (4.87)	3.88 (3.75)	—	1.94	4337
4b	69.62 (69.53)	5.18 (50.1)	3.45 (3.31)	—	1.96	4821
4c	64.18 (64.03)	4.65 (4.53)	3.25 (3.13)	3.72 (3.58)	1.96	5183

acryloyl chloride (i.e., acrylation) and the resultant products are called acrylated poly(ester-amide)s APEAs (4a–c). Their details are furnished in Table 2.

Preparation of Acrylated Poly(Ester-Amide)s-Methyl Methacrylate Monomer Blends (APEAs-MMA 5a–c)

When the acid value of APEAs resins (4a–c) fell below 55 mg KOH/gm, 0.05% of hydroquinone was added as an inhibitor. The whole reaction was stirred well for 10 min maintaining the temperature at 85°C. Then, 50% of APEAs and 50% of methyl methacrylate (MMA) monomer were mixed and stirred well at 80°C for 1 h. The resultant APEAs-MMA blends (5a–c) were obtained in the form of viscous syrup.

Composite Fabrication

Glass and carbon fiber composites of APEAs-MMA blends (5a–c) were prepared by the same method. Preparation method of glass fiber-reinforced composites (6a–c) and carbon fiber-reinforced composites (7a–c) for APEAs-MMA blends (5a–c) is given briefly as follows:

The composites were prepared by using E-type glass fiber cloth. The glass fiber: APEAs-MMA blend ratio is 60:40 (30%APEAs-MMA blends +10% DGEBF). Suspensions of APEAs-MMA blends (5a–c) and DGEBF were prepared in tetrahydrofuran (THF). In the above polymer suspension, 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 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 prepregs stacks were cured by heating then in an autoclave oven at 200°C for about 6 h. The composites so obtained were cooled to 45–50°C before the pressure was released.

Carbon fiber-reinforced composites (CFRC) have been prepared by using 30 tows (12 K) of carbon fiber. Then, by following the same method and molding conditions as above, carbon fiber-reinforced composites were obtained.

Table 3: DSC curing of APEAs-MMA blends (5a–c).

APEAs-MMA blends	Curing temperature (°C)			Activation energy (Ea) KJ/mol	Order of reaction 'n'
	Ti	Tp	Tf		
5a	105	130	148	123.7	1.76
5b	108	131	152	126.1	1.78
5c	111	138	158	130.1	1.94

Table 4: TGA of unreinforced cured samples of APEAs-MMA blends (5a–c).

	% Weight loss at various temps. (°C) from TGA				
APEAs-MMA blends	**150°C**	**300°C**	**450°C**	**600°C**	**750°C**
5a	2.06	10.78	63.06	78.04	84.06
5b	2.04	10.26	61.79	77.73	83.89
5c	2.03	10.03	58.89	73.04	80.23

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 [13]. The IR spectra were recorded in KBr pellets on a Nicollet 760 D spectrophotometer for both PEAs (3a–c) and APEAs (4a–c). Numbers of hydroxyl group present per repeat unit in PEAs (3a–c) were also determined by employing acetylating method [14]. Also, APEAs (4a–c) were characterized for the presence of double bonds per repeat unit, employing mercury-catalyzed bromate-bromide method [15]. All the results are furnished in Tables 1 and 2, respectively.

Curing

Curing of all APEAs-MMA blends (5a–c) was carried out in a Du Pont 900 DSC differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. 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°C min^{-1} heating rate. The sample weight used for this investigation was in the range of 4–5 mg. The results are furnished in Table 3.

Unreinforced cured samples of APEAs-MMA blends (5a–c) were subjected to thermogravimetric analysis (TGA) in Du Pont 950 thermogravimetric 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 of the composite samples against chemicals were measured according to ASTM D 543.

Table 5: Chemical, mechanical and electrical properties of composites based on APEAs-MMA blends.

Composite samples	% Change on exposure to 25% (W/V) NaOH		Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight					
GFRC 6a	1.1	1.09	396	417	406	89	22.04
GFRC 6b	1.0	1.07	399	419	416	96	22.54
GFRC 6c	0.98	1.03	402	422	423	99	23.02
CFRC 7a	1.4	1.16	392	411	396	81	20.98
CFRC 7b	1.3	1.14	395	413	397	83	21.13
CFRC 7c	1.3	1.13	399	416	393	85	21.5

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.

All mechanical and electrical tests were performed using three specimens and their results were averaged. The results are furnished in Table 5.

DISCUSSION

The C, H, N and S contents of all the PEAs (3a–c) and APEAs (4a–c) were consistent with their predicted structures and are furnished in Tables 1 and 2. The number average molecular weight of both PEAs (3a–c) and APEAs (4a–c) indicate that the degree of polymerization of both PEAs (3a–c) and APEAs (4a–c) is about 6. The IR spectra were consistent with the ones expected from the structures of the PEAs (3a–c) and APEAs (4a–c).

Numbers of hydroxyl group present per repeat unit in PEAs (3a–c) were analyzed. Also, APEAs (4a–c) were characterized for the presence of double bonds per repeat unit. Satisfactory results were found and the results are furnished in Tables 1 and 2, respectively.

Curing of all of these APEAs-MMA blends (5a–c) were carried out by using benzoyl peroxide as a catalyst. The data of DSC thermograms of all APEAs-MMA blends (5a–c) with activation energy and order of reaction are furnished in Table 3.

The unreinforced cured samples of APEAs-MMA blends (5a–c) were also analyzed by thermogravimetric analysis (TGA). The result reveals that the cured samples start their degradation at about 150°C and their 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° and 450°C and the products are lost completely beyond 750°C. TGA data of all the samples are shown in Table 4.

The glass and carbon fiber-reinforced composites of all APEAs-MMA blends (5a–c) were prepared and characterized for their chemical, mechanical and electrical properties. The results are furnished in Table 5. The results shows that composites have good chemical resistance and good mechanical and electrical strength.

CONCLUSIONS

From the characterizations of APEAs-MMA blends (5a–c) the following conclusions may be made.

Rather than using novel APEAs (4a–c), the blends of APEAs-MMA (5a–c) are more advantageous. The results furnished in Tables 3 to 5 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 glass fiber-reinforced composites have higher chemical resistance and mechanical properties than carbon fiber-reinforced composites. This is due to the unidirectional fibers in carbon composites. The results show that blends of APEAs-MMA monomer can be a competitor to commercial resins.

REFERENCES

[1] Shukla, V. *Pigment & Resin Techno.* **35**, 353 (2006).

[2] Samanta, B. C., Maity, T., Dalai, S., and Banthia, A. K. *Pigment & Resin Techno.* **37**, 3 (2008).

[3] Khambete, S. U.S. Patent, 7,290,300 (2007).

[4] Malik, M., Choudhary, V., and Varma, I. K. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **C40**, (2000).

[5] Pekarik, A. J. U.S. Patent, 4,840,980 (1989).

[6] Ahmad, S., Ashraf, S. M., Hasant, A., Yadav, S., and Jamal, A. *J. Appl. Poly. Sci.* **82**, 1855 (2001).

[7] Patel, H. S., and Panchal, K. K. *Int. J. of Poly. Mater.* **54**, 1 (2005).

[8] Patel, H. S., and Panchal, K. K. *Int. J. of Poly. Mater.* **54**, 795 (2005).

[9] Patel, H. S., and Patel, B. K. *Int. J. of Poly. Mater.* **56**, 312 (2009).

[10] Patel, H. S., and Panchal, K. K. *Poly. and Poly. Compo.* **12**, 519 (2004).

[11] Patel, H. S., and Panchal, K. K. *E- journal of Chem.* **1**, 32 (2004).

[12] Patel, T. B. (2007). Ph.D. Thesis, Veer Narmad University, Surat, India, Chap. 2, pp. 45–60.

[13] Patel, R. N., and Patel, S. R. *Angew. Makromol. Chem.* **96**, 85 (1981).

[14] Vogel, A. I. (1998). *Quantitative Organic Analysis*. CBS Publishers, New Delhi, pp. 677–679.

[15] Vogel, A. I. (1998). *Quantitative Organic Analysis*. CBS Publishers, New Delhi, pp. 765–766.