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Novel Flame-Retardant Acrylated Poly(Ester-Amide) Resins Based on Brominated Epoxy

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Bisphthalamic acids were prepared by reactions of phthalic anhydride and aromatic diamines. Novel flame-retardant poly(ester-amide) resins (FR-PEAs) were prepared by reactions of brominated epoxy resin (BER) with bisphthalamic acids using a base catalyst. The post reactions of these FR-PEAs were carried out with acryloyl chloride. The resultant products are designated as flame-retardant acrylated poly(ester-amide)s (FR-APEAs). The FR-PEAs and FR-APEAs were characterized by element analysis and number average molecular weight determined by nonaqueous conductometric titration. IR spectra for FR-PEAs and FR-APEAs were also carried out. The curing of these FR-APEAs was monitored on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. Glass fiber-reinforced composites of FR-APEAs have been fabricated and their chemical, mechanical, electrical and flame-retardant properties have been evaluated. The unreinforced cured samples of FR-APEAs were analyzed thermogravimetrically.

Keywords: bisphthalamic acids, brominated epoxy resin (BER), flame-retardant acrylated poly(ester-amide)s (FR-APEAs), laminates (composites), self-extinguishing time

INTRODUCTION

The fire resistance of materials is important to consider for the safety of individuals, and it must be taken into account at the beginning of the equipment development. Combustion resistance is improved by

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proper choice of resin and the use of fillers or flame-retardant additives. Included in this category are materials containing antimony trioxide, borate, phosphorus, bromine, and chlorine.

The fire behavior of composites can also be improved by using a halogenated resin in place of fillers. The effectiveness of the hydrogen halide decreases in the order of $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. Because organic iodines are thermally unstable, organic chlorides and bromides are generally used. Also many procedures exist to evaluate the fire behavior of the materials and structures [1,2].

It is well known that epoxy resins, polyamides and polyesters are independent polymer candidates for a wide range of industrial applications like composites, inks, paints, films and others [3–8]. Merging of these three epoxy, amide and ester segments into one polymer chain may yield a polymer with better properties than the individual ones along with flame retardancy.

Merging all three, i.e., epoxy, amide and ester, segments into one polymer chain has been reported recently from our laboratory [9,10]. Keeping this in mind, it was interesting to study the novel flame-retardant acrylated poly(ester-amide)s (FR-APEAs), based on brominated epoxy resin synthesized from tetrabromobisphenol-A and epichlorohydrin. In extension of this work [9,10] the present communication comprises the study of flame-retardant poly(ester-amide)s (FR-PEAs) (3a–c) based on reaction of bisphthalamic acids and brominated epoxy resin. Acrylation of all these FR-PEAs (3a–c) was carried out with acryloyl chloride; the resultant products are called flame-retardant acrylated poly(ester-amide)s, and are designated as (FR-APEAs) (4a–c). The synthetic steps are shown in Scheme 1.

EXPERIMENTAL

Materials

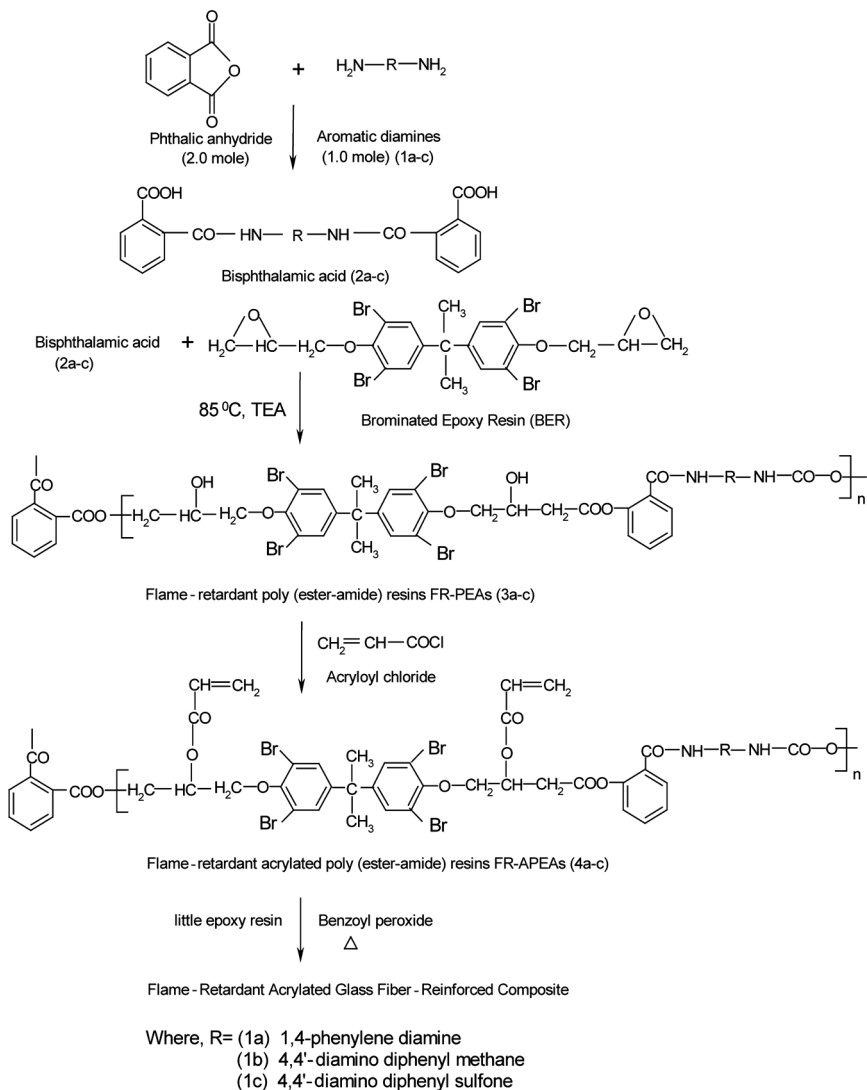
Commercially available brominated epoxy resin (BER) was obtained from ATUL Ltd.

The specifications of BER are:

1. Epoxy equivalent weight, 225–280.
2. Viscosity 750–1000 cps at 70°C.

The diamines used for bisphthalamic acids were:

- (1) 1, 4-phenylene diamine,
- (2) 4, 4'-diamino diphenyl methane and
- (3) 4, 4'-diamino diphenyl sulfone.



SCHEME 1 Synthesis steps.

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

Synthesis of Bisphthalamic Acids

The bisphthalamic acids were prepared by the simple reaction of phthalic anhydride and aromatic diamines (1a–c). These were prepared by using a method reported in the literature [11]. The general procedure is as follows.

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

Synthesis of Flame-Retardant Poly(Ester-Amide)s (FR-PEAs) and Flame-Retardant Acrylated Poly(Ester-Amide)s (FR-APEAs)

The bisphthalamic acids (2a–c) were then treated with brominated epoxy resin according to a method reported for reaction of epoxy resin and carboxylic group [12]. Brominated epoxy resin (1.0 mole) and bisphthalamic acids (2a–c) (1.0 mole) were charged in a three-necked flask equipped with a mechanical stirrer. To this, 8.0% of the above total above weight 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 as flame-retardant poly(ester-amide)s, FR-PEAs (3a–c) and their details are furnished in Table 1. Further reaction of these FR-PEAs was carried out with acryloyl chloride (i.e., acrylation) and the resultant products are called flame-retardant acrylated poly(ester-amide)s, designated as FR-APEAs (4a–c) and their details are furnished in Table 2.

TABLE 1 Characterization of FR-PEAs (3a–c)

FR-PEAs	Elemental analysis (Wt %) Calc./ (Found)				No. of -OH group per unit	No. average molecular wt. (\bar{M}_n) \pm 60
	%C	%H	%N	%S		
3a	45.18 (45.12)	3.34 (3.30)	2.92 (2.87)	—	1.96	5678
3b	49.33 (49.27)	3.63 (3.58)	2.67 (2.62)	—	1.95	6233
3c	45.98 (45.93)	3.28 (3.22)	2.55 (2.48)	2.91 (2.86)	1.95	6555

TABLE 2 Characterizations of FR-APEAs (4a–c)

FR-APEAs	Elemental analysis (wt %) Calc./(Found)				No. of double bonds per unit	No. of average molecular wt. (\bar{M}_n) \pm 60
	%C	%H	%N	%S		
4a	47.36 (47.29)	3.38 (3.31)	2.63 (2.59)	—	1.96	6355
4b	50.95 (50.89)	3.63 (3.59)	2.42 (2.36)	—	1.96	6887
4c	47.84 (47.81)	3.32 (3.28)	2.32 (2.27)	2.65 (2.59)	1.98	7171

Composite Fabrication

The composites were prepared by using glass fiber. The glass fiber: resin ratio is 60:40 (30%FR-APEAs+10% epoxy resin). Suspensions of FR-APEAs (4a–c) were prepared in tetrahydrofuran (THF). In the above polymer suspension, 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 \times 200 mm glass cloth and the solvent was allowed to evaporate. The 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 (0.4 MPa). The prepregs stacks were cured by heating them 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. The composites were then machined to final dimensions.

MEASUREMENTS

Elemental Analysis

The C, H, N and S content of all the FR-PEAs (3a–c) and FR-APEAs (4a–c) were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). The IR spectra were recorded in KBr pellets on a Nicollet 760 D spectrometer. The number average weight of all the FR-PEAs (3a–c) and FR-APEAs (4a–c) were estimated by nonaqueous conductometric titration following by a method reported in the literature [13]. Pyridine was used as a solvent and tetra-*n*-butylammonium hydroxide was used as a titrant. Their results are furnished in Tables 1 and 2, respectively. Numbers of hydroxyl group presents per repeating unit in FR-PEAs (3a–c) were also analyzed by employing acetylation method [14]. Also, FR-APEAs (4a–c) were characterized for presence of double bonds per repeat-unit, employing the mercury-catalyzed bromate-bromide method [15].

TABLE 3 DSC Curing of FR-APEAs (4a–c)

FR-APEAs	Curing temp. (T°C)		
	T _i	T _p	T _f
4a	111	140	191
4b	116	143	193
4c	120	149	197

Curing

Curing of all the FR-APEAs (4a–c) samples 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 instrument was calibrated using standard indium metal with known heat of fusion ($\Delta H = 28.45 \text{ J/g}$). Curing was carried out at 10°C per min heating rate. The sample weight for this investigation was in the range of 4–5 mg and an empty cell was used as a reference. The results are furnished in Table 3.

Unreinforced cured samples of FR-APEAs (4a–c) were subjected to thermo gravimetric analysis (TGA) on Du-Pont 950 thermogravimetric analyzer in air at a heating rate of 10°C per min. The results are furnished in Table 4.

COMPOSITE CHARACTERIZATIONS

Chemical Resistance Test

The resistance against chemicals of the composite samples was 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

TABLE 4 TGA of Unreinforced Cured Samples of FR-APEAs (4a–c)

FR-APEAs	% Weight loss at various temp. ($^\circ\text{C}$) from TGA				
	150 $^\circ\text{C}$	300 $^\circ\text{C}$	450 $^\circ\text{C}$	600 $^\circ\text{C}$	750 $^\circ\text{C}$
4a	2.00	15.75	48.77	91.44	96.79
4b	1.95	17.71	49.79	91.52	97.75
4c	1.27	19.52	50.44	92.75	95.75

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.

All mechanical and electrical tests were performed using three specimens and the average results are summarized in Table 6.

Flame Retardancy

The composites fabricated from FR-APEAs (4a–c) were analyzed for their flame retardancy. This property was measured by the self-extinguishing time according to ASTM D 635. In this test the major task is to measure the time between the removal of the sample from the burner and complete self-extinguishing of the sample. These were taken as an average of five specimens. The results are furnished in Table 6.

RESULTS AND DISCUSSION

The bisphthalamic acids were prepared by the reaction of phthalic anhydride (2.0 mole) and aromatic diamines (1.0 mole) (1a–c) following

TABLE 5 Chemical Resistance Properties of FR-APEAs (4a–c)

Reagents	% Change in FR-APEAs					
	4a		4b		4c	
	Thickness	Weight	Thickness	Weight	Thickness	Weight
H ₂ SO ₄	1.17	1.97	1.12	1.63	1.10	1.60
HCL	0.87	1.46	0.84	1.32	0.79	1.29
NaOH	0.83	1.23	0.71	1.12	0.71	1.07
Ethanol	0.32	0.34	0.22	0.35	0.19	0.32
Acetone	0.34	0.29	0.29	0.31	0.23	0.29
DMF	1.49	1.90	1.10	1.87	1.09	1.89
THF	0.93	0.89	0.69	0.79	0.63	0.77

TABLE 6 Mechanical, Electrical and Flame-Retardant Properties of Glass Fiber-Reinforced Composites of FR-APEAs (4a-c)

Composite samples of FR-APEAs	Flexural strength (MPa)	Impact strength (MPa)	Compressive strength (MPa)	Rockwell hardness (R)	Electrical strength in Air (kV/mm)	Self-extinguishing time (SET) (sec)
4a	398	437	407	71	20.3	23
4b	409	449	419	80	23.7	26
4c	414	467	433	92	26.9	27

a method reported in the literature [11]. The bisphthalamic acids (2a–c) were then treated with brominated epoxy resin according to the method reported for reaction of epoxy resin and carboxylic group [12]. The resultant FR-PEAs (3a–c) were then treated with acryloyl chloride, the resultant flame-retardant acrylated poly(ester-amide)s were designated as FR-APEAs (4a–c). The synthetic steps are shown in Scheme 1.

Both FR-PEAs (3a–c) and FR-APEAs (4a–c) were characterized by element analysis using Thermofinagan 1101 flash elemental analyzer (Italy). The values of C, H, N and S of each of the FR-PEAs (3a–c) and FR-APEAs (4a–c) were consistent with their predicted structures are furnished in Tables 1 and 2, respectively.

The number average molecular weight of both FR-PEAs (3a–c) and FR-APEAs (4a–c) was determined by nonaqueous conductometric titration, using a method reported in the literature [13]. The results are furnished in Tables 1 and 2, respectively. This indicates that the degree of polymerization of both FR-PEAs (3a–c) and FR-APEAs (4a–c) is about 6.

The IR spectra were consistent with the ones expected from the structures of the FR-PEAs (3a–c) and FR-APEAs (4a–c). FR-PEAs (3a–c) were characterized for the presences of hydroxyl groups by employing the acetylating method [14]. Also, FR-APEAs (4a–c) were characterized for the presence of double bonds by employing mercury-catalyzed bromate-bromide method [15].

Curing of all these FR-APEAs (4a–c) samples Was carried out and the data of DSC thermograms of the FR-APEAs (4a–c) are furnished in Table 3.

The unreinforced cured FR-APEAs (4a–c) products were analyzed by thermogravimetric analysis (TGA), to. The results reveal 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 15–19% is found at 300°C. However, the rate of decomposition increases very rapidly between 300 to 450°C and the products are lost completely beyond 750°C. TGA data of all the cured samples are shown in Table 4.

Glass fiber-reinforce composites of all FR-APEAs (4a–c) were prepared. The composites were characterized for their chemical resistance. The composites have good chemical resistance. The details are furnished in Table 5.

The glass fiber-reinforced composites of all FR-APEAs (4a–c) were also characterized for their mechanical and electrical resistances properties; the details are furnished in Table 6.

The glass fiber-reinforced composites of all FR-APEAs (4a–c) were also characterized for their flame retardancy. Their self-extinguishing time is well below 60 s and we can say that these composites of FR-APEAs resins have good flame retardancy. The details are furnished in Table 6.

CONCLUSIONS

The results of these novel FR-APEAs (4a–c) suggest that these resins can be competitors to commercial polyester resins because of their good chemical resistance, mechanical, electrical and flame-retardant properties. Further work in connection with blending of FR-PEAs (3a–c) and FR-APEAs (4a–c) with vinyl monomers is under progress.

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