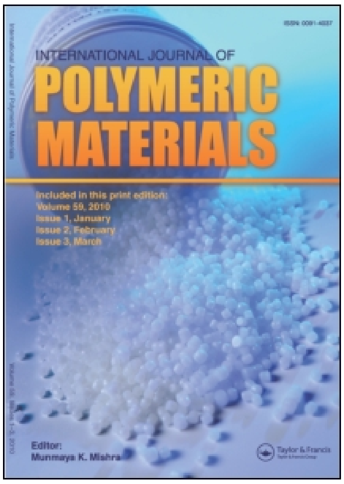

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Flame Retardant Unsaturated Poly(Ester Amide) Resins Based on Epoxy Resins

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Novel flame retardant unsaturated poly(ester amide) resins (FR-UPEAs) were prepared by the reaction of brominated epoxy resins (BER) with unsaturated aliphatic bisamic acids using a base catalyst. These FR-UPEAs were characterized by elemental analysis and number average molecular weight determination by non-aqueous conductometric titrations. The curing of these FR-UPEAs was carried out by using benzoyl peroxide (BPO) as a catalyst and was monitored on a differential scanning calorimeter (DSC). Based on DSC data, the glass fiber reinforced composites (i.e., laminates) of these FR-UPEAs have been fabricated and their chemical, mechanical, and electrical properties have been evaluated. The composites were analyzed for their self-extinguishing time. The unreinforced cured samples of FR-UPEAs resins were analyzed thermogravimetrically.

Keywords: brominated epoxy resin, flame retardant unsaturated polyester amide resins, bisamic acid, differential scanning calorimeter, thermogravimetrically, self extinguishing time.

INTRODUCTION

Some methods for obtaining flame retardant polyesters were described by Nametz [1] and Lyon [2]. Although the use of special additives (chlorinated paraffins, phosphorus, and halogen derivatives) was initially adopted, it was later suggested [2–3] that modified polyesters

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based on built-in reactive groups by used in order to overcome the gradual diffusion of the additives into the atmosphere.

The flammability mechanism of polyesters and other polymeric systems has been extensively analyzed [4–9], as was the specific role of the halogens in flame retardancy [1,2,4,10–12]. It is claimed that the halogens serve as radical scavengers, converting the radicals produced during the burning of the polymer into halide radicals of lower activity. It has been stated that the brominated products have an advantage over their chlorinated counterparts [2] due to the weaker bond strength of the former (65 kCal/mole in the C−Br bond compared with 81 kcal/mole for the C−Cl bond).

Keeping this in mind, it was thought interesting to study the novel flame retardant unsaturated poly(ester-amide) resins based on brominated epoxy resins synthesized from tetrabromobisphenol-A and epichlorohydrin.

It is well known that epoxy resins, polyamides, and unsaturated polyester resins (UPEs) are independent polymer candidates for a wide range of industrial applications, such as composites, inks, paints, films, and so on [13–22]. Merging all the three, epoxy, amide, and UPE segments, into the polymer chains has not received attention academically and technically. Merging of these three segments into one polymer chain may yield a polymer with better properties than those of the individual ones along with an additional property of flame retardancy. Thus it was thought interesting to study the novel unsaturated

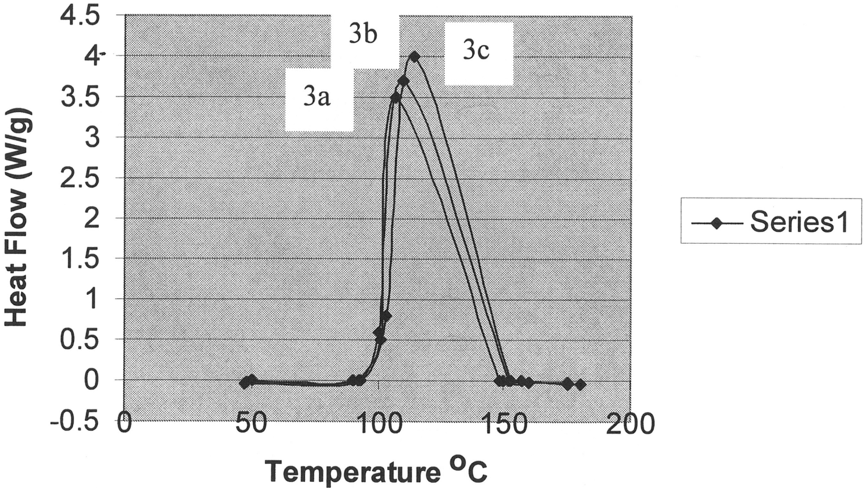
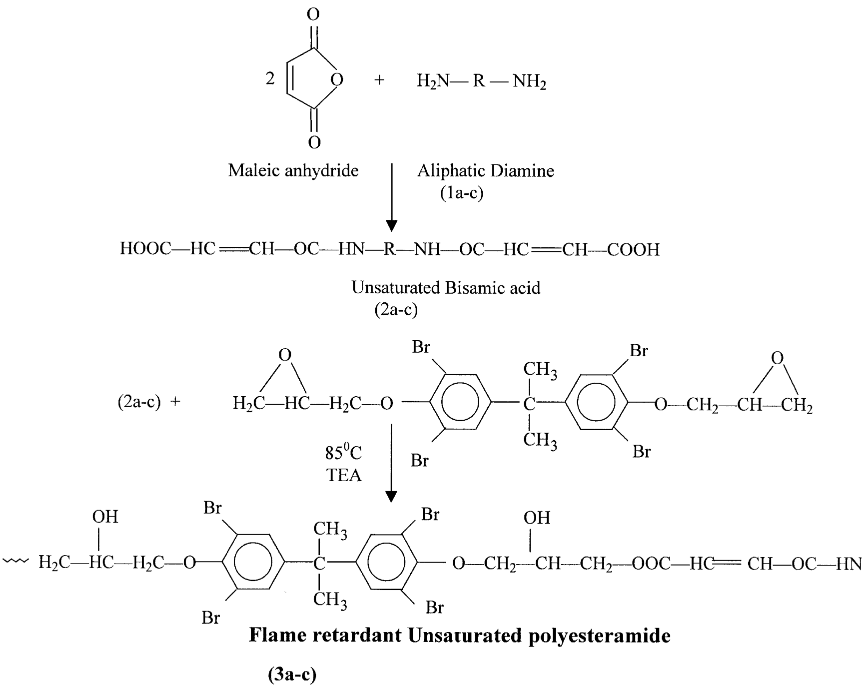


FIGURE1 DSC thermogram of FR-UPEA resins.



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

poly(ester amide) resin. The present article comprises the synthesis of flame retardant unsaturated poly(ester-amide) resin based on epoxy resin (FR-UPEAs). The synthetic work is presented in Scheme 1, and their DSC traces are presented in Figure 1.

EXPERIMENTAL

Materials

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

The specifications of BER are: (1) Epoxy equivalent weight is 225–280 and (2) Viscosity at 70°C is 750–1000 cps.

The diamines used for the synthesis of unsaturated bisamic acids are: (1) 1,2-Ethylene diamine, (2) 1,3-Propylene diamine, and (3) 1,6-Hexamethylene diamine.

The diamines were obtained from Diamines Chemicals, Nandesari. All the other chemicals used were of laboratory grade.

Synthesis of Unsaturated Bisamic Acids

The unsaturated bisamic acids were prepared by a method reported in the literature [23,24]. The general procedure is as follows:

To a well-stirred solution of maleic anhydride (2.0 mole) in acetone, a solution of diamine (mentioned earlier) (1.0 mole) in acetone was gradually added at 0–5°C. The addition of diamine is completed within half an hour. The resulting bisamic acid was filtered, washed with acetone, and air-dried. The structures of the three-bisamic acids (now designated as unsaturated bisamic acids) are given in Scheme 1. The unsaturated bisamic acids were obtained in the form of a free-flowing powder and are designated as (2a–c).

Synthesis of Flame Retardant Unsaturated Poly(ester amide) Resin (UPEA)

Brominated epoxy resin (BER) (1.0 mole) and unsaturated bisamic acid (1.0 mole) (2a–c) were changed in a three-necked flask equipped with a mechanical stirrer. To this, triethylamine (TEA) (8% of total weight of the above) was added as a catalyst. The resulting mixture was slowly heated up to 85°C along with continuous stirring. A sample was taken at regular intervals to check the acid value. The reaction was continued till the acid value fell below 60 mgKOH/gm. The resin was then discharged to give flame retardant unsaturated poly(ester-amide) resins.

All the three resins were obained in the form of reddish pink semisolid mass and were designated as (3a–c). Their details are furnished in Table 1.

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

UPEA sample	Elemental analysis (wt%) Calc./Found %C	%H	%N	No. of double bonds	IR spectral features (cm^{-1}) –OH	$-CH_2$	–COO	Number average molecular weight ($\overline{M}n$)
3a	40.52 (40.46)	3.75 (3.69)	1.75 (1.68)	1.0	3500–2600	2850–2920	1680	4074
3b	41.29 (41.17)	3.93 (3.81)	1.72 (1.66)	1.0	3500–2600	2850–2920	1680	4404
3c	43.47 (43.32)	4.44 (4.31)	1.63 (1.57)	1.1	3500–2600	2850–2920	1680	4559

COMPOSITE FABRICATION

The composites were prepared by using glass fiber having the fiber: resin ratio of 60:40. (30% FR-UPEA resin + 10% BER.)

Suspensions of FR-UPEAs (3a–c) were prepared in terahydrofuran (THF). To each such syrup 1% of ethylene dimethacrylate and 0.05% of benzoyl peroxide (BPO) was added. This syrup was well stirred for about 5 min. The suspension mixture was applied with a brush to a 150 mm × 150 mm glass fiber plies and the solvent was allowed to evaporate. The dried fiber plies were stacked on top of one another and pressed between steel plates coated with a Teflon release sheet and compressed in a flat platen under 70 psi pressure. Keeping them in an autoclave oven maintained at their respective curing temperature for about 6 h cured this prepreg stack. The composites so obtained were cooled to 50°C before the pressure was released. The composites were then machined to final dimensions.

MEASUREMENTS

The C, H, and N contents of all the FR- UPEAs (3a–c) were estimated by means of a Carlo Erba elemental analyzer (Italy). The IR spectra were recorded in KBr pellets on a Nicolet 400 D spectrophotometer. Their data are presented in Table 1.

Number average molecular weights of all the FR-UPEAs were estimated by non-aqueous conductometric titration following the method reported in the literature [25]. Pyridine was used as a solvent and tetra-n-butyl ammonium hydroxide was used as a titrant. The results are furnished in Table 1.

Curing

Curing of FR-UPEA resins (3a–c) was carried out by using benzoyl peroxide (BPO) as a catalyst and was monitored on a differential scanning calorimeter (DSC). A Du Pont High Pressure DSC-9900 Thermal Analyzer was used for this study. The instrument was calibrated using standard indium metals with known heats 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 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 2.

Unreinfornced cured samples were subjected to thermogravimetric analysis (TGA) on a Du Pont 990 Thermal Analyzer MK-III in air at a heating rate of 10°C min^{-1}. The results are furnished in Table 3.

TABLE 2 DSC Curing Data of Flame Retardant Unsaturated Polyester Amide Resins (3a–c)

FR-UPEA sample	Curing temp. (T°C) T_i	T_p	T_f
3a	101	107	148
3b	100	110	152
3c	103	114	153

COMPOSITE CHARACTERIZATION

Chemical Resistance Test

The resistances against chemicals of the composite were measured according to ASTM D 543. The specimen dimensions were 20 mm × 20 mm. The chemicals used for the study were H_2SO_4 (25%v/v), HCl (25%v/v), NaOH (25%w/v) ethanol, acetone, THF, and DMF. The test was performed by dipping the composite sample 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 the percentage change in thickness and weight. The results are furnished in Table 4.

Mechanical Testing

All mechanical testing was performed using three test specimens and their average results are furnished in Table 5.

- The compressive strength was measured on a model A-74-37 Universal Instron testing machine at room temperature according to ASTM D 695.

TABLE 3 TGA of Unreinforced Cured Sample of FR-UPEAs Resins

	% Weight loss at various temp. (°C) from TGA				
UPEA sample	150	300	450	600	750
3a	4.95	12.22	51.92	66.13	80.03
3b	4.89	12.17	51.90	66.03	79.97
3c	4.83	12.10	51.85	66.00	79.98

TABLE 4 Chemical Resistance Properties of FR-UPEA Resins (3a–c)

FR-UPEA samples Reagents	% Change 3a Thickness	 3a Weight	 3b Thickness	 3b Weight	 3c Thickness	 3c Weight
H_2SO_4	1.12	1.84	1.14	1.85	1.17	1.88
HCl	0.89	1.23	0.90	1.25	0.92	1.28
NaOH	0.75	1.12	0.78	1.16	0.81	1.20
Ethanol	0.21	0.36	0.23	0.39	0.27	0.42
Acetone	0.19	0.32	0.22	0.35	0.26	0.40
DMF	1.13	1.91	1.16	1.92	1.19	1.96
THF	0.55	0.77	0.62	0.82	0.65	0.86

- Notched Izod impact strength was measured on a Zwick model no. 8900 impact tester machine at room temperature, according to the method of ASTM D 256.
- The Rockwell hardness was measured on a Rockwell hardness tester model RAS/Saro Engg. Pvt. Ltd. at room temperature according to ASTM D 785.

Electrical Testing

The measurement of the dielectric strength was carried out on a high voltage tester machine oil test set.

Flame Retardant Properties

The composites fabricated from FR-UPEA resins were analyzed for their flame retardant properties. The property was measured by the self-extinguishing time method according to ASTM D-635. In this test

TABLE 5 Mechanical, Electrical, and Flame Retardant Properties of Glass Fiber Reinforced Composites of UPEA Resins (3a–c)

UPEA composite	Impact strength (MPa)	Compressive strength (MPa)	Rockwell hardness (R)	Electrical strength in air (kV/mm)	Self extinguishing time (SET) (sec)
3a	405	396	78	19.9	21
3b	408	395	74	20.6	23
3c	414	390	70	21.5	30

the major task is to measure the time elapsed between the removal of the sample from the burner and complete self-extinguishing of the sample. This was taken as the average time for 10 standard specimens of 150 mm × 20 mm each. Satisfactory results are considered when these times are below 60 s. The results are furnished in Table 5.

RESULTS AND DISCUSSION

The bisamic acids were obtained by the reaction of maleic anhydride and diamine following the reported method [23–24]. The bisamic acids were then treated with brominated epoxy resin (BER) (a commercial epoxy resin) using a base catalyst. The resultants UPEAs were then characterized by elemental analysis. The values of C, H, and N of each UPEA were consistent with its predicted structure. The unsaturation was also determined by following the bromate–bromide titration method [26] and confirmed one double bond per repeat unit. The number average molecular weight ($\overline{\text{M}}$n) of these resins was determined by non-aqueous conductometric titration [25] and the values of ($\overline{\text{M}}$n) are furnished in Table 1. This indicates that the $\overline{\text{DP}}$ of these polymers is about 6. The IR spectra (not shown) of all UPEAs show the prominent positions of important segments in the polymer chain: A broad band from 3600–2500 cm^{-1} with inflexions at 2850 cm^{-1} and 2920 cm^{-1}. This broad band is mainly due to secondary $-$OH groups. The strong band at 1100 cm^{-1} supports this. The inflexions arise from $-\text{CH}_2$ groups present in both epoxy and aliphatic diamines. The bands due to presence of aliphatic segments are at their expected positions. The discernible difference between the spectra of epoxy resin and UPE reveals that the band at 910 cm^{-1} in the spectrum of epoxy group is almost vanished in the spectra of UPEAs and a new band appears at 1680 cm^{-1} from ester group. Also, a peak is observed at 550 cm^{-1}, which is attributed to C$-$Br bond. This confirms the reaction between BER and bisamic acid.

The UPEA resins (3a–c) were cured by using benzoyl peroxide as a catalyst and their curing study was monitored on a differential scanning calorimeter. The data of DSC thermograms of all the resins are furnished in Table 2.

The unreinforced cured UPE resins (3a–c) products were also analyzed thermogravimetrically (TGA). TGA data of all the cured samples are shown in the Table 3. The results reveal that the cured samples start their degradation at about 150°C and their initial weight loss is about 5%. This weight loss may be due to either insufficient curing of components used or due to the catalyst used. A weight loss of about 12% is found at 300°C. However, the rate of decomposition increases very rapidly between 300°C to 450°C and the products are lost completely beyond 850°C.

The glass fiber reinforced composites of all UPEA resins (3a–c) were also prepared based on DSC data. The composites were characterized for their chemical resistance test. They have good resistance toward common solvents like ethanol and acetone. These results are furnished in Table 4. They were also characterized for their mechanical tests and the results are furnished in Table 5. They were tested for flame resistance and the results are furnished in Table 5. Their self extinguishing time is well below 60 s and, hence, they have a good resistance to fire. The electrical strength is between 19.5 to 21.5 kv/mm. Results are furnished in Table 5.

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