

## Synthesis and Studies on Interacting Blends of Acrylated Poly(Ester-Amide) Resins – II 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)s (PEAs) was prepared by reaction of epoxy resin (DGEBF) with bisphthalamic acids. Acrylation of PEAs was carried out using acryloyl chloride and products are designated as acrylated poly(ester-amide)s (APEAs). PEAs and APEAs were characterized by elemental analysis and number average molecular weight. IR spectra recorded for PEAs. Blending of APEAs was carried out with methyl methacrylate monomer. Curing of APEAs-MMA blends was monitored on differential scanning calorimeter. Composites of APEAs-MMA blends have been laminated and characterized. Unreinforced cured samples of these APEAs-MMA blends were analyzed thermogravimetrically.

**Keywords:** Aliphatic diamines, Bisphthalamic acids, Epoxy resin of Bisphenol-F (DGEBF), Poly(ester-amide)s (PEAs), Acrylated Poly(ester-amide)s (APEAs), APEAs-MMA blends,

### Introduction

It is well known that epoxy resins, polyesters and polyamides are the most widely used independent polymer candidates for a wide range of industrial applications like paints, inks, composites, films and so on<sup>1-5</sup>. Merging of all three *i.e.* epoxy, ester and amide segments into one polymer chain have been recently reported from our laboratory<sup>6</sup>. Thermoplastic modification via blending or by the addition of the other thermoset is another possibility in order to improve the chemical, mechanical and electrical properties<sup>7,8</sup>. Blending of these thermoplastics is very useful in order to improve hardness and brittleness of the materials. Several works in direction of blending in order to improve some properties have been also reported with methyl methacrylate and styrene monomer<sup>9</sup>. In extension of this work the present article comprises the synthesis and study on blending of novel acrylated poly(ester-amide) resins (APEAs) with methyl methacrylate monomer. The synthetic steps are shown in Scheme 1.

## Experimental

Commercially available diglycidylether of bisphenol-F (DGEBF) was obtained from ATUL Ltd. Its epoxy equivalent weight is 160. The aliphatic diamines used for the preparation bisphthalamic acids were, 1,2-ethane diamine, 1,3-propane diamine and 1,6-hexamethylene diamine.

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 g.m<sup>-2</sup> were used for composite fabrication. All other chemicals used were of pure grade.

### *Synthesis of bisphthalamic acids*

The bisphthalamic acids were prepared by a simple addition reaction of phthalic anhydride and aliphatic diamine (**1a-c**). These were prepared by using method reported in the literature<sup>6,9-12</sup>. The general procedure for the synthesis of bisphthalamic acid is as follows.

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

### *Synthesis of PEAs (3a-c) and APEAs (4a-c)*

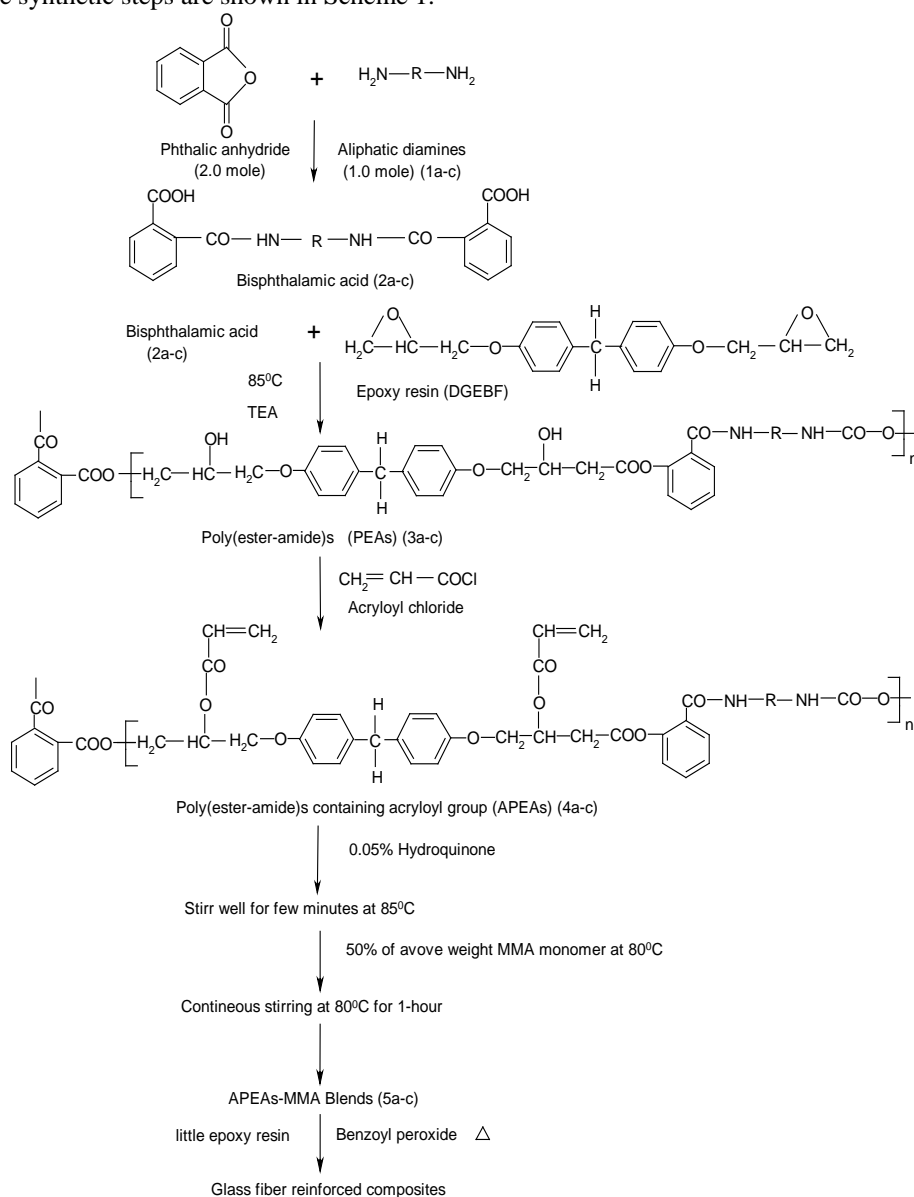
Both PEAs and APEAs were prepared by a reaction between epoxy resin (DGEBF) and bisphthalamic acid (**2a-c**). These were prepared by using method reported in the literature<sup>6,9-12</sup>. The bisphthalamic acids (**2a-c**) were then treated with epoxy resin (DGEBF) according to the method reported for reaction of epoxy group and carboxylic group<sup>13</sup> using a base catalyst. The general procedure for the synthesis of bisphthalamic acid is as follows.

Epoxy resin (DGEBF) (1.0 mole) and bisphthalamic acid (**1a-c**) (1.0 mole) were charged in 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 up to 85 °C with continuous stirring. The reaction temperature was maintained at 85 °C and a sample was taken at regular intervals to check the acid value employing carboxyl end group analysis method. The reaction was continued till the acid value fell below 60 mg KOH/g. The resin was also analyzed for negative epoxy value test using reported method<sup>1</sup>. The resultant resins were then discharged and are called poly(ester-amide) resins, designated as (PEAs) (**3a-c**) and their details are furnished in Table 1. All PEAs resins were also characterized for the hydroxyl number per repeating unit employing acetylating method<sup>14</sup>. The results revealed the presence of two -OH group per repeating unit for all the resins. The results are furnished in Table 1. Further reaction of all these PEAs resins was carried out with acryloyl chloride (*i.e.* acrylation) and resultant products are called acrylated poly(ester-amide) resins, designated as APEAs resins (**4a-c**). The unsaturation was also determined by following the bromate-bormide titration method<sup>15</sup> and confirmed two double bonds per repeating unit. The results of unsaturation measurement of all APEAs resins are furnished in Table 2.

### *Synthesis of APEAs-MMA monomer Blends (5a-c)*

The APEAs-MMA monomer blends were prepared by using method reported in literature<sup>9-12</sup>. The general procedure for the preparation of APEAs-MMA monomer blends is as follows.

When the acid value of APEAs resins (**4a-c**) fell below 60 mg KOH/g, 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 the total weight of the above, 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-MMA blends (**5a-c**). The synthetic steps are shown in Scheme 1.



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

**Scheme 1**

### Composite fabrication

The composites were prepared by using glass fiber. The glass fiber: APEAs-MMA blend ratio is 60:40 (30%APEAs-MMA blend + 10% Epoxy resin). Suspensions of APEAs-MMA blend were prepared in dimethylformamide (DMF). In the suspension of above polymer 1% of ethylene dimethylacrylate (as a cross linked) 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 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 “Teflon” film release sheet and compressed in a flat platen under 70 psi pressure. This prepared stack was cured by keeping it in an autoclave oven at 225 °C for about 6 hour to cure this prepared stack. 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 content of all the PEAs resins (**3a-c**) and APEAs resins (**4a-c**) were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). The IR spectra were recorded in Kerr pellets on a Nicollet 760 D spectrometer. The data are presented in Tables 1 and 2 respectively. The number average weight of all the PEAs and APEAs were estimated by non-aqueous conductometric titration following by method reported in the literature<sup>9-12</sup>. Pyridine was used as a solvent and tetra-*n*-butyl ammonium hydroxide was used as a titrant. The results are furnished in Table 1 and 2 respectively.

**Table 1.** Characterization of PEAs Resins (**3a-c**)

PEAs ( <b>3a-c</b> )	No. of –OH group per repeating unit	Elemental analysis (Wt %) Calc. / (Found)			IR spectral features, cm <sup>-1</sup>			No. average molecular weight ( $\overline{M}_n$ ) ± 60
		%C	%H	%N	-OH	-CH <sub>2</sub>	-COO	
<b>3a</b>	1.93	63.82 (63.70)	5.67 (5.58)	4.96 (4.83)	3500- 2600	2850- 2920	1680	3341
<b>3b</b>	1.93	64.35 (64.20)	5.88 (5.69)	4.84 (4.76)	3500- 2600	2850- 2900	1680	3430
<b>3c</b>	1.95	65.80 (65.68)	6.45 (6.34)	4.51 (4.39)	3500- 2600	2850- 2900	1680	3666

**Table 2.** Characterization of APEAs Resins (**4a-c**)

APEAs ( <b>4a-c</b> )	Elemental analysis (Wt %) Calc. / (Found)			No. of double bonds per repeating unit	No. average molecular weight ( $\overline{M}_n$ ) ± 60
	%C	%H	%N		
<b>4a</b>	64.28 (64.01)	5.35 (5.17)	4.16 (3.93)	1.95	3992
<b>4b</b>	64.72 (64.42)	5.53 (5.30)	4.08 (3.86)	1.91	4069
<b>4c</b>	65.93 (65.60)	6.04 (5.85)	3.84 (3.67)	1.90	4309

### Curing

Curing of all these APEAs-MMA blends were carried out on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. A Due 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 °C min<sup>-1</sup> 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.

**Table 3.** DSC Curing of APEAs-MMA Blends (**5a-c**)

APEAs-MMA blends ( <b>5a-c</b> )	Curing temperature, T °C		
	Ti	Tp	Tf
<b>5a</b>	122	148	163
<b>5b</b>	119	131	148
<b>5c</b>	126	163	179

Unreinforced cured samples of APEAs-MMA blends were subjected to thermogravimetric analysis (TGA) on Due Pont 950 thermo gravimetric analyzer in air at a heating rate of 10 °C min<sup>-1</sup>. The results are furnished in Table 4.

**Table 4.** TGA of unreinforced cured samples of APEAs-MMA Blends (**5a-c**)

APEAs-MMA Blends ( <b>5a-c</b> )	% Weight loss at various temps. (°C) From TGA				
	150 °C	300 °C	450 °C	600 °C	750 °C
5a	1.70	10.05	49.73	77.80	83.37
5b	1.76	10.83	49.80	77.79	82.41
5c	1.97	10.13	58.27	78.11	84.61

### Composite characterizations

#### Chemical resistance test

The resistance against Chemicals of the composites was measured according to ASTM D 543. The results are furnished in Table 5.

**Table 5.** Chemical, mechanical and electrical properties of glass fiber reinforced composites of APEAs-MMA blends

Composite Samples of APEAs-MMA Blends ( <b>5a-c</b> )	Chemical Resistance	Flexural Strength (MPa)	Compressive Strength (MPa)	Impact Strength (MPa)	Rockwell Hardness (R)	Electrical Strength in air (kV/mm)
	Thickness	Weight				
<b>5a</b>	1.19	1.01	436	417	421	97
<b>5b</b>	1.20	1.02	441	426	435	105
<b>5c</b>	1.24	1.00	454	439	448	112

#### Mechanical 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 average results are summarized in Table 5.

## Results and Discussion

The bisphthalamic acids were prepared by the reaction of phthalic anhydride (2.0 mole) and aliphatic diamines (1.0 mole) (**1a-c**) following by the method reported in the literature<sup>6,9-12</sup>. The bisphthalamic acids (**2a-c**) were then treated with epoxy resin (DGEBF) according to the method reported for reaction of epoxy group and carboxylic group<sup>13</sup> using a base catalyst. The resultant products are called poly (ester-amide) resins and are designated as PEAs (**3a-c**). The resultant PEAs resins (**3a-c**) then treated with acryloyl chloride, the resultant products are called acrylated poly(ester-amide) resins and designated as APEAs resins (**4a-c**). The synthetic steps are shown in Scheme 1.

Both PEAs resins and APEAs resins were characterized by elemental analysis using Thermofinagan 1101 flash elemental analyzer (Italy). The values of C, H, N of each of the PEAs resins and APEAs resins were consistent with their predicted structures. The results of elemental analysis for both PEAs resins and APEAs resins are furnished in Table 1 and 2 respectively.

The number average molecular weight of both PEAs resins and APEAs resins were determined by non-aqueous conductometric titration, using method reported in literature<sup>6,9-12</sup>. The results of number average molecular weight for both PEAs resins and APEAs resins are furnished in Table 1 and 2 respectively. This indicates that the degree of polymerization of both PEAs resins and APEAs resins is about 6.

The IR spectra of all PEAs resin show the prominent position of important segments in the polymer chain. The broad band from 3600-2500  $\text{cm}^{-1}$  with inflexions at 2850-2920  $\text{cm}^{-1}$  this broad band mainly due to secondary -OH groups. This is supported by the strong band at 1100  $\text{cm}^{-1}$ . The inflexions are raised from -CH<sub>2</sub> 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  $\text{cm}^{-1}$  appeared in the spectrum of epoxy groups is almost vanished in the spectra of PEAs resins and a new band appear at 1680  $\text{cm}^{-1}$  from ester group. This confirms the reaction between DGEBF 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.

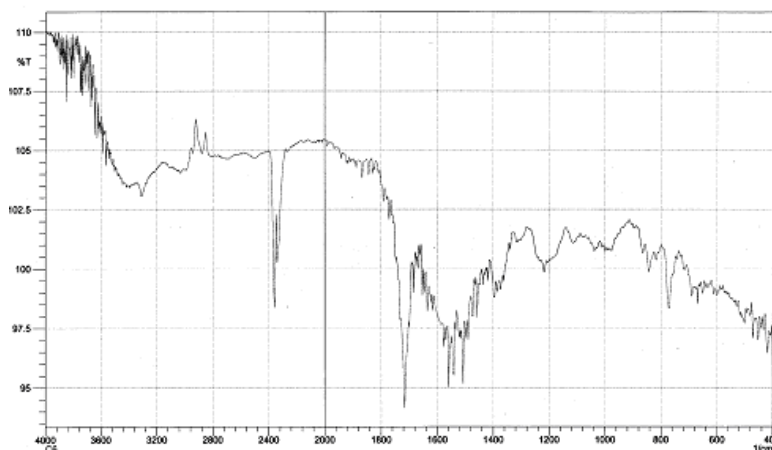
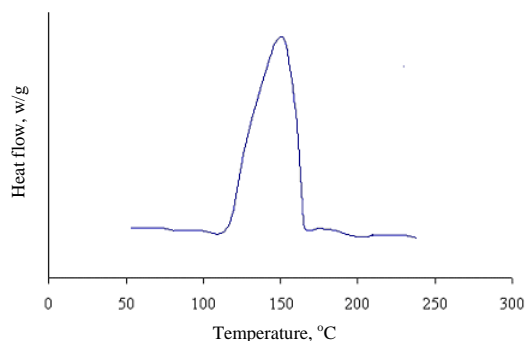


Figure 1. IR spectra of sample (**3a**)

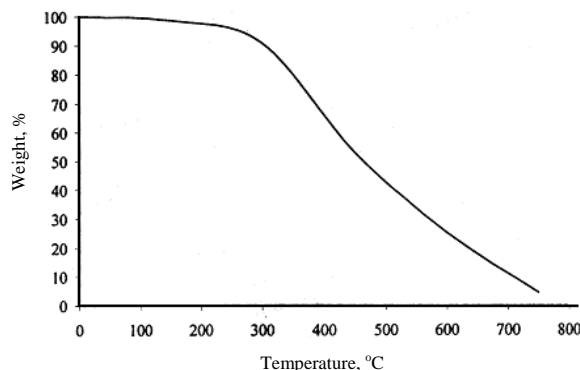
Also acrylation of all PEAs (**3a-c**) resin was carried out. Completion of this reaction between PEAs resins and acryloyl chloride was determined by elemental analysis and number average molecular weight. All the PEAs resins were characterized for the presence of hydroxyl group per repeating unit employing acetylating method<sup>14</sup>. The results revealed the presence of two -OH group per repeating unit for all the resins. The results are furnished in Table 1. The unsaturation presents in APEAs (**4a-c**) resin was also determined by following the bromate-bormide titration method<sup>15</sup> and confirmed two double bonds per repeating unit. The results of unsaturation measurement of all APEAs resins are furnished in Table 2.

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



**Figure 2.** DSC of sample (**5c**)

The unreinforced cured samples of APEAs-MMA 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 10% 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 750 °C. TGA data of all the cured samples are given 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-MMA blends (**5a-c**) were prepared based on their DSC data. The composites were characterized for their chemical resistance test, mechanical and electrical tests. Their results are furnished in Table 5. The results shows that composites have good chemical resistant property, good mechanical and electrical strength.

## Conclusion

The results of these novel APEAs-MMA blends suggest that these blends can be competitor to commercial polyester resins because of their good chemical resistance properties, good mechanical and electrical strength. Further work in connections with the blending PEAs resins and APEAs resins with other vinyl monomers is under progress.

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