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INTERACTING BLENDS OF NOVEL ACRYLATED UNSATURATED POLYESTERS BASED ON DGEBA WITH STYRENE MONOMER

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ABSTRACT

Novel unsaturated polyesters (PEs) were prepared by reaction of epoxy resin of bisphenol-A with various glutaconic acids using a base catalyst. The post reactions of all these PEs were carried out with acryloyl chloride. The resultant products are designated as acrylated polyesters (APEs). The PEs and APEs were characterized by elemental analysis. Number average molecular weights were determined by non-aqueous conductometric titration method. IR spectra of PEs and APEs were also recorded. Blending of these APEs were carried out with styrene monomer. The curing of these APEs-styrene blends was monitored on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. Based on DSC data, the glass fiber reinforced composites of APEs-styrene blends have been fabricated and their chemical, mechanical and electrical properties have been evaluated. The unreinforced cured samples of APEs-styrene blends were analyzed thermogravimetrically.

Keywords: Epoxy resin (DGEBA), Polyester, Polyamide, Number average molecular weight ($\overline{M}_n$), Differential scanning calorimeter (DSC), Thermogravimetric analysis (TGA), Interacting blends.

INTRODUCTION

It is well known that epoxy resins, polyesters and polyamides are independent polymer candidate for a wide range of industrial applications like composites, adhesive, anticorrosive coatings and others[1-5]. Merging of these two epoxy and ester segments into one polymer chain may yield a polymer with better properties than those of the individual ones.

Hence, in extension of our earlier work[6,7], the present article comprises the study of APEs-styrene blends. This has been presented in Scheme 1.

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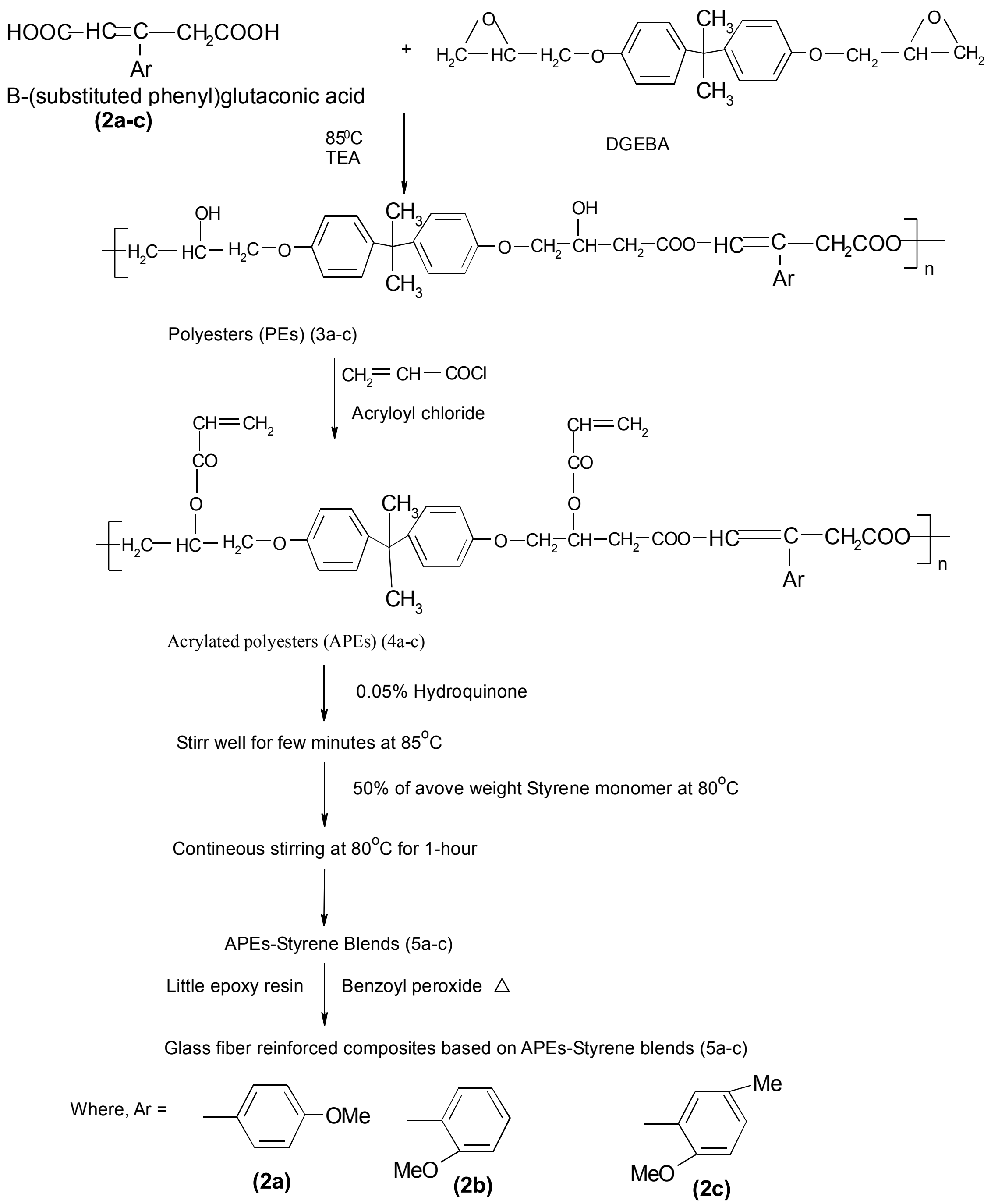

Scheme 1: Synthesis steps

EXPERIMENTAL

Materials

Epoxy resin based on bisphenol-A was prepared according to reported method.[8] Plane weave fibers, in the form of E-glass woven fabric (polyester) compatible) 0.25 mm thick (Unnati Chemicals, India) of a real weight 270 g m^{-2} were used for composite fabrication. All other chemicals used were of pure grade.

Synthesis of bisphthalamic acids

Various glutaconic acids were prepared by method reported in literature.[9]

Synthesis of PEs and APEs

Both PEs **(3a-c)** and APEs **(4a-c)** were prepared by method reported in an earlier communication.[10,11]

Composite fabrication

The composites were prepared by using E-type of glass fiber. The glass fiber : resin ratio is 60 : 40 (30% APEs resin + 10% DGBC). Suspensions of APEs **(4a-c)** were prepared in tetrahydrofuran. In the suspension of above polymer, 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 prepgregs prepared in this way were then stacked one on top of another and pressed between steel plates coated with a “Teflon” film release sheet and compressed under 70 psi pressure. The prepgregs stacks were cured by heating it in an autoclave oven at 220^{o}C for about 6 hours. The composites so obtained were cooled to 45-50^{o}C before the pressure was released. The composites were then machined to final dimensions.

Measurements

Elemental analysis

The C, H, N and S contents of all the PEs **(3a-c)** and APEs **(4a-c)** were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). The number average molecular weight of all thePEs and APEs were estimated by non-aqueous conductometric titration.[10] The IR spectra were recorded in Kerr pellets on a Nicollet 760 D spectrometer for both PEs and APEs. Number of hydroxyl groups present per repeating unit in PEs **(3a-c)** were analyzed by employing acetylating method reported earlier.[10] Also, APEs **(4a-c)** were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method reported.[10] All the results for number of –OH group for PEs and presence of double bonds for APEs were found to be consistent with the predicted structures and the results are furnished in Tables 1 and 2, respectively.

Table 1: Characterization of PEs (3a-c)

PEAs	Elemental analysis (Wt %) Calc. / (Found)		No. of –OH group per repeating unit	Number average molecular weight ($\overline{M}_n$) ± 60
	% C	% H		
3a	68.75 (68.72)	6.25 (6.16)	1.93	3516
3b	68.75 (68.69)	6.25 (6.18)	1.95	3516
3c	69.1 (69.07)	6.44 (6.38)	1.94	3600

Table 2: Characterization of APEs (4a-c)

APEs Samples	Elemental analysis (Wt %) Calc. / (Found)		No. of double bonds per repeating unit	Number average molecular weight ($\overline{M}_n$) ± 60
	% C	% H		
4a	68.42 (68.36)	5.84 (5.77)	1.97	4164
4b	68.42 (68.38)	5.84 (5.79)	1.95	4164
4c	68.76 (68.69)	6.01 (5.94)	1.98	4248

Curing of all these APEs-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^{0}C at 10^{0}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.

Table 3: DSC curing of APEs-styrene blends (5a-c)

APEs-Styrene blends	Curing temperature (^{0}C)		
	Ti	**Tp**	**Tf**
5a	107	136	158
5b	113	143	164
5c	116	149	170

Unreinforced cured samples of APEs-styrene blends **(5a-c)** were subjected to thermogravimetric analysis (TGA) on Du-Pont 950 thermo gravimetric analyzer in air at a heating rate of 10^{0}C min^{-1}. The sample weight used for this investigation was in the range of 4-5 mg. The results are reported in Table 4.

Table 4: TGA of unreinforced cured samples of APEs-styrene blends (5a-c)

APEs-styrene blends	% Weight loss at various temps. (^{o}C) from TGA				
	150^{o}C	**300^{o}C**	**450^{o}C**	**600^{o}C**	**750^{o}C**
5a	1.82	9.86	61.15	76.56	80.28
5b	1.60	9.66	59.57	75.35	79.94
5c	1.43	9.62	56.84	71.14	78.56

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 the percentage changes in thickness and weight. The results are given in Table 5.

Table 5: Chemical resistance properties of APEs-styrene blends (5a-c)

Reagents	% Change in APEs-styrene blends (5a-c)					
	5a		5b		5c	
	Thickness	Weight	Thickness	Weight	Thickness	Weight
H_2SO_4	1.07	1.83	1.14	1.83	1.13	1.87
HCl	0.83	1.24	0.87	1.24	0.23	1.29
NaOH	0.70	1.07	0.76	1.16	0.82	1.16
Ethanol	0.22	0.34	0.27	0.35	0.28	0.37
Acetone	0.18	0.28	0.25	0.37	0.28	0.35
DMF	1.06	1.86	0.18	1.94	0.19	1.94
THF	0.52	0.73	0.63	0.78	0.64	0.84

Mechanical and electrical testing

(i) Flexural strength was measured according to ASTM D 790.

(ii) Compressive strength was measured according to ASTM D 695.

(iii) Impact strength was measured according to ASTM D 256.

(iv) Rockwell hardness was measured according to ASTM D 785.

(v) Electrical strength was measured according to ASTM D 149.

The results are summarized in Table 6.

Table 6: Mechanical and electrical properties of APEs-styrene blends (5a-c)

Composites of APEs-styrene blends (5a-c)	Flexural strength (MPa)	Impact strength (MPa)	Compressive strength (MPa)	Rockwell hardness (R)	Electrical strength in air (kV/mm)
5a	395	404	398	86	21.3
5b	398	411	393	83	21.6
5c	399	415	392	82	21.9

All mechanical and electrical tests were performed using three specimens and their average results were considered.

RESULTS AND DISCUSSION

Novel polyesters (PEs) were prepared by reaction of epoxy resin of bisphenol-A with bisphthalamic acids using a base catalyst. The post reactions of all these PEs were carried out with acryloyl chloride. The resultant products are designated as acrylated polyesters (APEs). Both PEs and APEs were prepared by method reported earlier.[10] The blends of APEs-Styrene blends were prepared by reported method.[11]

The C, H, N and S content of all the PEs **(3a-c)** and APEs **(4a-c)** were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). These results are furnished in Tables 1 and 2, respectively. From the results, it is clear that values of C, H, N and S of each PEs and APEs were consistent with their predicted structures. The number average molecular weight of all the PEs and APEs were estimated by non-aqueous conductometric titration.[10] The results are reported in Tables 1 and 2, respectively. The IR spectra were recorded in KBr pellets on a Nicollet 760 D spectrometer for both PEs and APEs. The IR spectra of all PEs and APEs were consistent with their predicted structures.

Number of hydroxyl groups present per repeating unit in PEs **(3a-c)** was also analyzed by employing acetylating method.[10] Also, APEs **(4a-c)** were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method.[10] Satisfactory results were found and the results are furnished in Tables 1 and 2, respectively.

Curing of all these APEs-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 data of DSC thermograms of all APEs-styrene blends **(5a-c)** are furnished in Table 3.

The unreinforced cured samples of APEs-styrene blends **(5a-c)** were also analyzed by thermogravimetric analysis (TGA). The results reveal that the cured sample starts their degradation at about 150^0C 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% was found at 300^0C. However, the rate of decomposition increases very rapidly between 300^0C to 450^0C and reach up to 61% and the products are lost completely beyond 750^0C. TGA data of all the cured samples are shown in Table 4.

The glass fiber reinforced composites of all APEs-styrene blends **(5a-c)** were prepared based on their DSC data. The composites were characterized for their chemical resistance test and results are reported in Table 5. The composites were also characterized for their mechanical and electrical tests. Their results are given in Table 6. The results show that composites have good chemical resistant property, good mechanical and electrical strength.

CONCLUSIONS

From the characterizations of APEs-styrene blends, the following conclusions have been drawn. Rather than using novel APEs, the blends of APEs-styrene is 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 also show that blends of APEs-styrene monomer can be competitor to commercial polyester resins.

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