

Research Paper

INTERACTING BLENDS OF NOVEL ACRYLATED POLYESTERS BASED ON DGEBA AND S-TRIAZINE CONTAINING BIS ACID

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Novel polyesters (PEs) were prepared by reaction of various 4,4'-(6-alkoxy-1,3,5-triazine-2,4-diyl) bis(oxy)dibenzoic acid(1a-c) with epoxy resin of bisphenol-c using a base catalyst. The post reactions of all these PEs were carried out with acryloyl chloride. The resultant products were designated as acrylated polyesters (APEs). The PEs and APEs were characterized by elemental analysis, number average molecular weight determined by non-aqueous conductometric titration method. IR spectra of PEs and APEs were also recorded. Blending of these APEs were carried out with methyl acrylate monomer. The curing of these APEs-Methyl acrylate 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-Methyl acrylate blends have been fabricated and their chemical, mechanical and electrical properties have been evaluated. The unreinforced cured samples of APEs-Methyl acrylate blends were analyzed thermo gravimetrically.

Keywords: Epoxy resin (DGEBC), Polyester, Number average molecular weight (Mn), Differential scanning calorimeter (DSC), Thermo gravimetric analysis (TGA), Interacting blend

INTRODUCTION

It is well known that epoxy resins, and polyesters are independent polymer candidates for a wide range of industrial application like composites, adhesive, anticorrosive coatings and others (V Shukla, 2006; B C Samanta *et al.*, 2008; S Ahmad, 2001; V Thulasiraman, 2009; M Malik, 2000). Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones and are

available in a wide range of molecular weights from several hundreds to tens of thousands. Epoxy resins belong to the most important thermosetting polymers with good heat, moisture and chemical resistance, toughness, electrical and mechanical strength and good adhesion to many substrates. The linear epoxy is cured into three-dimensional cross-linked networks by curing agents to give a hard and infusible

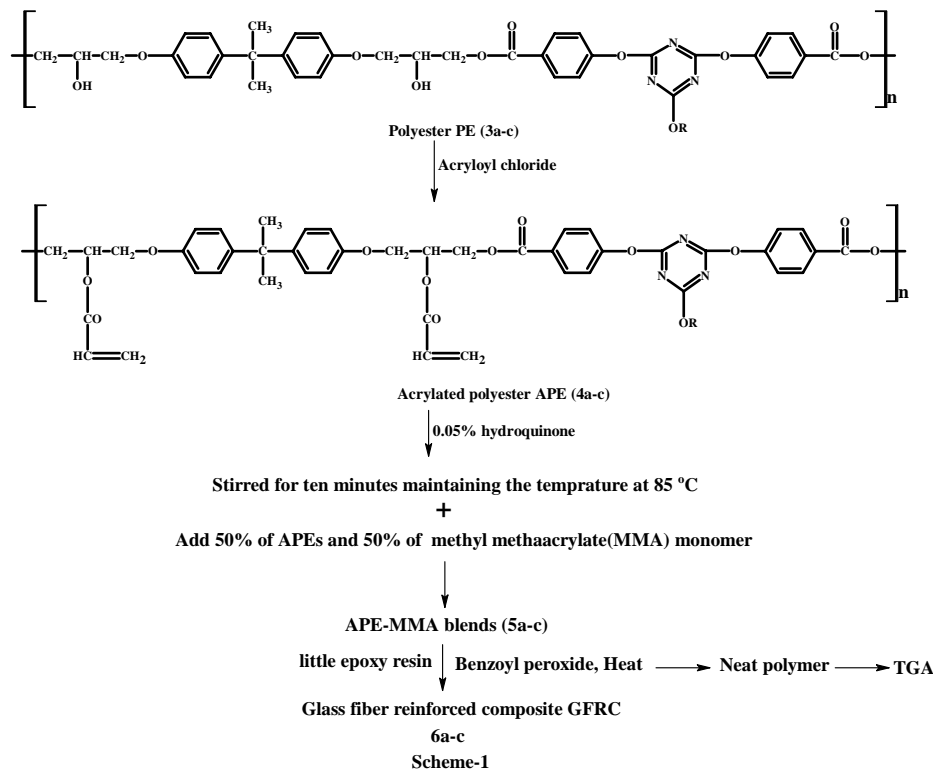
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thermoset resin. These cured polymers are applicable to surface coatings, painting materials, composites, laminates, encapsulates for semiconductors and insulating materials for electrical devices. Recently much attention has been made to modify the structural make-up of epoxy resins in the attempts to enhance the flexibility and toughness as well as thermal properties of the final product (E Balcerzak and H Janeczak, 2004; K Xu *et al.*, 2004). An example is the incorporation of long hydrocarbon chain with intermittent ether bond into the polymer backbone (L Wang and C P Wong, 2000). This modification did affect flexibility to the resin but at the expense of a lowered glass transition. Introducing a saturated cycloaliphatic ring into the backbone structure was previously attempted (L Wang and C P Wong, 2000; G H Kwak, 2000; M

Xie *et al.*, 2001). s-Triazine ring containing derivatives have been reported as reactive dyes and some are also used as polymers and drugs (H S Freeman and J F Esancy, 1991; J A Chaudhari *et al.*, 2006; and 2007). As phenyl hydrazine derivatives containing s-triazine ring are not reported so far. The present work carried out in this context (R P Patel *et al.*, 2007; J A Chaudhari, 2009). Such type of derivative also reported as DGEBA epoxy resin curing agent (J A Chaudhari and R P Patel, 2010; R P Patel and J A Chaudhari, 2010). Merging of these epoxy and s-triazine segments into one polymer chain may yield a polymer with better properties than these of the individual ones. The present article comprises the study of APEs-Methyl acrylate blends. This has been scanned in Scheme 1.

Figure 1: Schematic Diagram



MATERIALS AND METHODS

Materials

Epoxy resin based on bisphenol-c was prepared according to method reported (P H Parsania *et al.*, 1985). Plane weave fibers, in the form of E-glass woven fabric (polyester) compatible 0.25mm thick 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 4, 4'-(6-alkoxy-1, 3, 5-triazine-2,4-diyl)bis(oxy)dibenzoic acid(1a-c) were prepared by method reported from our laboratory (D Limya and V Bhave, 1931).

Synthesis of (PEs) and (APEs)

Both PEs (3a-c) and APEs (4a-c) were prepared by method reported in literature (H S Patel and B K Patel, 2009).

Synthesis of APEs-Methyl Acrylate Blends (5a-c)

These were prepared by method reported in literature (H S Patel and B K Patel).

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%DGEBC). 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 200mm x 200mm 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" film release sheet and compressed under 70 psi pressure. The prepregs stacks were cured

by heating it in an autoclave oven at 220°C for about 6 hour. 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 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 the PEs and APEs were estimated by non-aqueous conductometric titration following method reported in an earlier communication H. (S Patel and B K Patel, 2009). 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) was analyzed by employing acetylating method reported (S Patel and B K Patel, 2009). In addition, APEs (4a-c) were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method reported (S Patel and B K Patel, 2009). All the results for number of -OH group for PEs and presence of double bonds for APEs are found to be consistent with the predicted structures and the results are furnished in Table 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 (Mn) ± 60
	%C	%H		
3a	64.72(64.69)	5.15(5.14)	1.95	3678
3b	65.12(65.10)	5.33(5.31)	1.93	3753
3c	65.50(65.48)	5.50(5.47)	1.92	3826

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

AEAs	Elemental analysis (Wt %)(Calc. / Found)		No. of double bonds per repeating unit	Number average molecular weight (Mn) ± 60
	%C	%H		
	4a	65.50(65.48)		
4b	65.82(65.80)	5.64 (5.63)	1.97	4449
4c	66.13 (66.12)	5.78(5.75)	1.95	4495

Curing

Curing of all these APEs-Methyl acrylate 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 ($\Delta H=28.45J/g$). 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 along with an empty reference cell. The results are furnished in Table 3. Unreinforced cured samples of APEs-Methyl acrylate blends (5a-c) were subjected to thermogravimetric analysis (TGA) on Du-Pont 950 thermo gravimetric analyzer in air at a heating rate of 100C min⁻¹. The sample weight used for this investigation was in the range of 4-5 mg. The results are furnished in Table 4.

Table 3: DSC curing of APEs-Methyl Acrylate Blends (5a-c)

APEs-Methyl acrylate blends	Curing Temperature (°C)		
	Ti	Tp	Tf
	5a	104	132
5b	112	137	158
5c	113	145	165

Table 4: TGA of Unreinforced Cured Samples of APEs-Methyl Acrylate Blends (5a-c)

APEs-Methyl acrylate blends	% Weight loss at various temps. (°C) from TGA				
	150°C	300°C	450°C	600°C	750°C
5a	1.84	9.87	61.15	76.58	80.31
5b	1.63	9.66	59.58	75.36	79.94
5c	1.45	9.62	56.85	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 H2SO4 (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 100mL 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 furnished in Table 5.

Table 5: Chemical Resistance Properties of APEs-Methyl Acrylate Blends (5a-c)

Re-agents	% Change in APEs-Methyl acrylate blends (5a-c)					
	5a		5b		5c	
	Thick-ness	Weight	Thick-ness	Weight	Thick-ness	Weight
Acetone	0.18	0.26	0.23	0.34	0.25	0.32
Ethanol	0.19	0.31	0.25	0.36	0.26	0.38
DMF	1.07	1.84	0.18	1.92	0.16	1.94
THF	0.50	0.74	0.61	0.78	0.61	0.81
NaOH	0.70	1.08	0.77	1.13	0.80	1.16
H ₂ SO ₄	1.08	1.80	1.12	1.83	1.13	1.85
HCl	0.81	1.21	0.86	1.24	0.21	1.27

Mechanical and Electrical Testing

- (1) The Electrical strength was measured according to ASTM D 149.
- (2) The Impact strength was measured according to ASTM D 256.
- (3) The Compressive strength was measured according to ASTM D 695.
- (4) The Rockwell hardness was measured according to ASTM D 785.
- (5) The Flexural strength was measured according to ASTM D 790.

The results are furnished in Table 6. All mechanical and electrical tests were performed using three specimens and their average results were considered.

Compos-ites of APEs-Methyl acrylate blends (5a-c)	Compres-sive Strength (MPa)	Electrical Strength in air (kV/mm)	Flexural Strength (MPa)	Impact Strength (MPa)	Rockwell Hardness (R)
5a	393	21.1	388	402	82
5b	389	21.3	390	405	84
5c	386	21.7	394	409	83

RESULTS AND DISCUSSION

Novel polyesters (PEs) were prepared by reaction of epoxy resin of bisphenol-C with 4,4'-(6-alkoxy-1,3,5-triazine-2,4-diyl)bis(oxy)dibenzoic acid(1a-c) 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 in an earlier communication (M Xie *et al.*, 2001). The blends of APEs-Methyl acrylate blends were prepared by method reported in literature (H S Patel and B K Patel).

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). Their results are furnished in Table 1 and 2 respectively. From the results, we can say 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 following by method reported in an earlier communication (H S Patel and B K Patel, 2009). Their results are furnished in Table 1 and 2 respectively. The IR spectra were recorded in Kerr 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 reported in an earlier communication (H S Patel and B K Patel, 2009). Also, APEs (4a-c) were characterized for the presence of double bonds per repeating unit employing mercury-catalyzed bromate-bromide method reported in an earlier communication (H S Patel and B K Patel, 2009). Satisfactory results were found and the results are furnished in Table 1 and 2 respectively. Curing of all these APEs-Methyl acrylate 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-Methyl acrylate blends (5a-c) are furnished in Table 3. The unreinforced cured samples of APEs-Methyl acrylate blends (5a-c) were also analyzed by thermo gravimetric analysis (TGA). The result reveals that the cured sample starts their degradation at about 1500C 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

3000C. However, the rate of decomposition increases very rapidly between 3000C to 4500C and reach up to 61% and the products are lost completely beyond 7500C. TGA data of all the cured samples are shown in Table 4. The Glass fiber reinforced composites of all APEs-Methyl acrylate blends (6a-c) were prepared based on their DSC data. The composites were characterized for their chemical resistance test their results are furnished in Table 5. The composites were also characterized for their mechanical and electrical tests. Their results are furnished in Table 6. The results shows that composites have good chemical resistant property, good mechanical and electrical strength.

CONCLUSION

From the characterizations of APEs-Methyl acrylate blends the following conclusions have been made. Rather than using novel APEs the blends of APEs-Methyl acrylate is more advantageous. The results furnished in Table 3 to 6 itself suggests 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 show that blends of APEs-Methyl acrylate monomer can be competitor to commercial polyester resins.

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