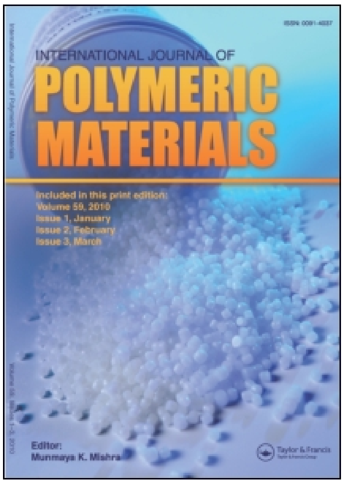

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Novel Interacting Blends of Unsaturated Polyester-s-Triazine and Epoxy Resin

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2-(4-ethyl-1-piperazinylo)-4,6-bismaleatedethylamino-1,3,5-triazine (EBT) was prepared by the reaction of 2-(4-ethyl-1-piperazinylo)-4,6-bishydroxyethylamino-1,3,5-triazine and maleic anhydride. The EBT derivative was characterized by elemental analysis, acid value and spectral studies.

EBT was then polycondensed respectively with three commercial epoxy resins, namely diglycidyl ether of bisphenol-A (DGEBA), diglycidyl ether of bisphenol-F (DGEBF) and diglycidyl ether of bisphenol-C (DGEBC). The resultant polymers are designated as unsaturated polyester-s-triazine (UPETs) and were characterized by elemental analysis, spectral study, molecular weight determination, differential scanning calorimeter (DSC)and thermogravimetry. The interacting blends of UPETs with DGEBA epoxy resin was made at stoichiometric ratio. The blending of these systems was monitored on a differential scanning calorimeter (DSC), and based on DSC data the glass-reinforced composites (GRC$_s$) were prepared and characterized by physical and mechanical properties.

Keywords DSC, epoxy resin (DGEBA, DGEBF, DGEBC), glass-reinforced composites, IR and spectral study, maleic anhydride, thermogravimetry, unsaturated polyester-s-triazine (UPETS)

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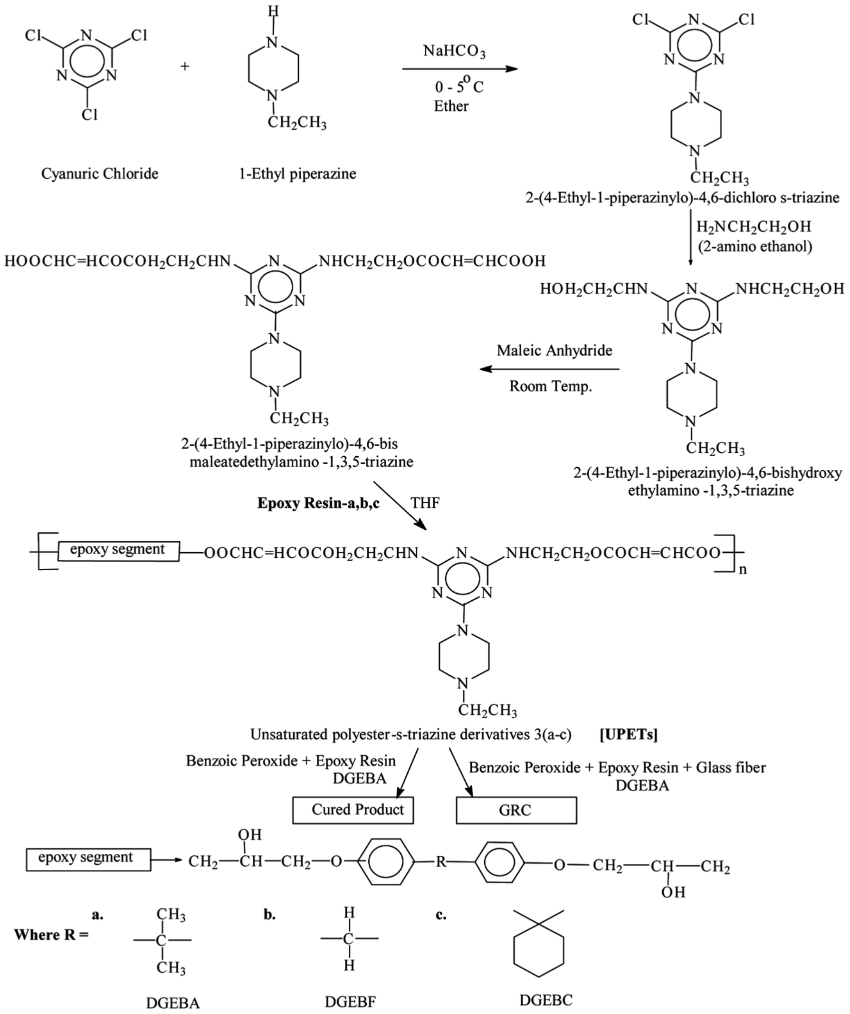
INTRODUCTION

A number of derivatives containing the s-triazine ring have been reported as heterocyclic compounds [1–3]. They are applicable mostly as reactive dyes and some are used as polymers and drugs [4]. The aryl hydrazine derivatives containing the s-triazine ring were reported by us recently [5–7]. In this context, one author (JAC) reported the piperazinylo bisaryl hydrazino-s-triazine derivatives and their application as epoxy resin curing agents [8]. Thus in continuation of this work, the present paper comprises the novel interacting blends of unsaturated polyester-s-triazine and epoxy resin. The research work is shown in Scheme 1.



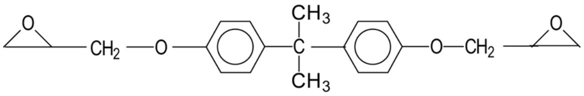
Scheme 1: Preparation of UPETs.

EXPERIMENTAL

Materials

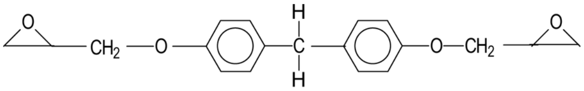
Cyanuric chloride, maleic anhydride and aminoethanol were obtained as Analar grade from a local dealer. 2-(4-ethyl-1-piperazinylo)-4,6-dichloro-1, 3,5-triazine was prepared by reported method [8]. All other chemicals used were of laboratory grade. Epoxy resins, namely diglycidyl ether of bisphenol-A (DGEBA) and diglycidyl ether of bisphenol-F (DGEBF), were obtained from a local market, and diglycidyl ether of bisphenol-C (DGEBC) was prepared in the laboratory as per the method of DGEBA [9]. The specifications of epoxy resin are as follows:

a. Epoxy Resin DGEBA equivalent weight 190, viscosity at 25°C 9000–12000 cps



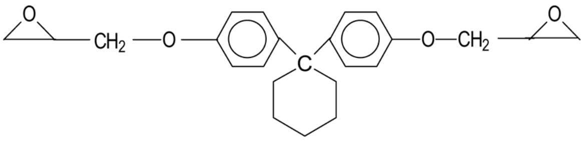
Epoxy resin [DGEBA]

b. Epoxy Resin DGEBF equivalent weight 175, viscosity at 25°C 15000–17000 cps



Epoxy resin [DGEBF]

c. Epoxy Resin DGEBC equivalent weight 210, viscosity at 25°C 11000–12000 cps



Epoxy resin [DGEBC]

Glass cloth : E-type of glass cloth woven fabric [poly (ester amide) compatible] 0.25 mm thick (Unnati Chemicals, India) of a real weight 270 $g \cdot m^{-2}$ was used for composite fabrication.

Procedures

Synthesis of 2(4-ethyl-1-piperazinylo)-4,6-bishydroxyethylamino-1,3,5-triazines (PHS)

To a well stirred solution of 2-(4-ethyl-1-piperazinylo)-4,6-dichloro-1,3,5-triazine (0.01 mole) in tetrahydrofuran (THF) solvent (50 ml) a solution of aminoethanol (0.02 mole) in THF (50 ml) was added gradually at room temperature. The mixture was stirred for 2 h. Then the mixture was refluxed for an additional 2 h. The resultant solid product was filtered, washed with THF and air-dried.

Elemental Analysis: $C_{13}H_{25}N_7O_2$(M.W. 311)

Molecular formula	Mol. weight	% C		% H		% N	
		Cald.	**Found**	**Cald**	**Found**	**Cald**	**Found**
$C_{13}H_{25}N_7O_2$	311	50.16	50.01	8.03	7.087	31.51	31.46

IR Features:	
$3200-3600\,cm^{-1}$	OH
$3400\,cm^{-1}$	NH
$1450, 2850, 2920\,cm^{-1}$	CH_2
$3030, 1500, 1600\,cm^{-1}$	Aromatic
$2950, 1370\,cm^{-1}$	CH_3
$1510, 1250, 870\,cm^{-1}$	s-triazine

NMR: δ ppm

3.1 to 3.4 (12H) triplet of CH_2 of N-CH_2

3.6 (4H) triplet of CH_2 of N-CH_2OH

3.65 (2H) triplet of OH of CH_2OH

1.02 (3H) triplet of CH_3 of CH_2CH_3

2.4 (2H) quartret of CH_2 of CH_2CH_3

-NH hump not visible

Synthesis of 2-(4-ethyl-1-piperazinylo)-4,6-bismaleatedethylamino-1,3,5-triazine (EBT)

To a well-stirred solution of 2(4-ethyl-1piperazinylo)-4,6-bishydroxyethylamino-1,3,5-triazine and maleic anhydride (0.02 mole) were added at room temperature. A few drops of pyridine was added and the mixture was refluxed for 6 h. The resultant mixture was poured into water. The ppts were collected, washed and air-dried. It was a solid amorphous powder m.p. 207.8°C (uncorrected).

Elemental Analysis: $C_{21}H_{29}N_7O_8$(M.W. 507)

Molecular formula	Mol. weight	% C		% H		% N	
		Cald.	**Found**	**Cald.**	**Found**	**Cald.**	**Found**
$C_{21}H_{29}N_7O_8$	507	49.70	49.56	5.71	5.56	19.32	19.37

Acid Value:

- Theoretical: 220.9 mg KOH/1 g. Sample
- Found: 218.1 mg KOH/1 g. Sample

IR Features:		
	1680 cm^{-1}	COOH
	3400 cm^{-1}	NH
	1450, 2850, 2920 cm^{-1}	CH_2
	2980, 1370 cm^{-1}	CH_3
	1700 cm^{-1}	ester
	1510, 1250, 870 cm^{-1}	s-triazine

NMR: δ ppm

1.02 (3H) triplet of CH_3 of CH_2CH_3

2.38 (2H) quartret of CH_2 of CH_2CH_3

3.1 to 3.4 (8H) triplet of CH_2 of CH_2CH_2

3.7 (4H) triplet of CH_2 of CH_2NH

4.55 (4H) triplet of CH_2 of CH_2O

6.3 (2H) doublet of CH of CHCO

6.5 (2H) doublet of CH of CHCOOH

11.2 (2H) singlet OH of -COOH

-NH hump not visible

Synthesis of Unsaturated Polyester-s-triazines Derivatives 3(a-c) [UPETs]

Epoxy resin (DGEBA, DGEBF and DGEBC) (1.0 mole) and 2-(4-ethyl-1-piperazinylo)-4,6-bismaleatedethylamino-1,3,5-triazine [1.0 mole] were changed in a three-neeked flask equipped with a mechanical stirrer. To this, 1 ml triethylamine (TEA) was added as a catalyst. The resulting mixture was slowly heated up to 85°C along with continuous stirring. All the three resins were obtained in the form of a pasty mass and were designated as (3a-c). Their details are furnished in Table 1. All the UPETs(3a-c) compounds listed in Table 1 were dark yellow amorphous powders.

MEASUREMENTS

The elemental analysis of all (3a-c) compounds were determined by TF flash EA 1101. The FTIR spectra of (3a-c) compounds were scanned in KBr pallets on a Perkin Elmer FTIR spectrophotometer [10–12]. The NMR spectra were scanned on a Perkin Elmer FT-NMR spectrophotometer.

COMPOSITES FABRICATION

A suspension mixture of DGEBA epoxy resin and UPETs(3a-c) at stoichiometrc ratio suspended in tetrahydrofuran was prepared and 10 mg benzoic peroxide (BPO) was added, then stirred well for 2 to 5 min. The suspension was applied with a brush onto a 150 mm × 150 mm epoxy-compatible fiber glass cloth and the solvent was allowed to evaporate. Once dried, the 10 plies of prepreg thus prepared were stacked one on top of another, pressed between steel plates coated with a Teflon film release and compressed in a flat platen press under about 70 psi pressure. The prepreg stack was cured by heating in the press to 120°–140°C for 12 h. The composites so obtained was cooled to 45°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions. All the chemical, mechanical and electrical tests were conducted according to the ASTM or IS methods [13].

Mechanical Testing

All mechanical testing was performed using specimens and their average results appear in Table 2. The compressive strength was measured according to the IS method at room temperature.

Curing

Curing interacting blends of UPET$_S$(3a-c) with DGEBA epoxy resin was carried out by using benzoic peroxide (BPO) as a catalyst [14] and on a differ-

Table 1: Characterization of unsaturated polyester-s-triazines derivatives (3a-c).

Compound	Molecular formula	Mol. weight	% C		% H		% N	
			Cald.	Found	Cald.	Found	Cald.	Found
3a	$C_{42}H_{53}N_7O_{12}$	847	59.50	59.35	6.2	6.20	11.57	11.42
3b	$C_{40}H_{49}N_7O_{12}$	819	58.60	58.45	5.98	5.85	11.96	11.81
3c	$C_{45}H_{57}N_7O_{12}$	887	60.87	60.72	6.42	6.28	11.04	10.90

Table 2: Mechanical and electrical properties of GRC based on UPET$_S$(3a-c)-DGEBA epoxy resin.

GRC	UPET$_S$(3a-c)-DGEBA epoxy resin	Specific gravity	Impact strength (Mpa)	Compressive strength (Mpa)	Rockwell hardness (R)	% Change on exposure to 25% W/v NaOH	
						Thickness	Weight
1	3a	1.88	287	195	90	1.0	1.0
2.	3b	1.99	276	205	99	1.0	1.0
3	3c	1.91	246	198	117	1.0	1.2

Table 3: Curing characteristic of UPET$_S$(3a-c)-DGEBA epoxy resin systems (1 : 1) at 10°C / min.

UPET$_S$(3a-c)-DGEBA epoxy resin system	**Kick-off temperature T_i (°C)**	**Peak temperature T_p (°C)**	**Final temperature T_f (°C)**	**Activation energy (Ea) (K cal/mol)**	**Order of reaction**
3a	121	160	168	33.07	1.11
3b	105	147	166	30.02	1.09
3c	112	155	164	31.02	0.92

Table 4: TGA of unreinforced cured materials of UPET$_S$(3a-c)-DGEBA epoxy resin.

UPET$_S$(3a-c)-DGEBA epoxy resin	% Weight loss at various temp. C^0				
	200	300	400	500	600
3a	4.1	14	62	87	99
3b	4.2	13	61	89	98
3c	4.5	14	62	87	98

ential scanning calorimeter (DSC) [15]. A Du Point High Pressure DSC-900 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 30^0–300°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 3.

Unreinforced cured samples were subjected to thermogravimetric analysis (TGA)[16,17] on a Perkin Elmer USA Pyres TGA-1 in a slow stream of air at a heating rate of 10°C min^{-1}. The results are furnished in Table 4.

RESULTS AND DISCUSSION

The reaction between maleic anhydride and 2-(4-ethyl-1-piperazinylo)-4,6-bishydroxyethylamino-1,3,5-triazine is facile. The product (3a-c) is dark yellow amorphous powder. Analytical data are consistent with the predicated structures. The C,H,N contents of all (3a-c) shown in Table 1 are consistent with the predicated structures shown in Scheme 1. The IR spectra of all (3a-c) are almost identical. All the IR spectra comprise important features mentioned in an experimental part. All features are consistent with the presence group. The UPET$_S$ were also cured with benzoic peroxide (BPO), but the resultant mass was not properly hard material even though the temperature was up to 150°C. Hence the curing of UPET$_S$ was attempted with DGEBA resin. The unreinforced cured epoxy resin (3a-c) products were also analyzed thermogravimetrically (TGA). TGA data of all the cured samples are shown in the Table 4 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 300^0 to 450°C, and the products are lost completely beyond 850°C.

The crosslinking of epoxy resin by various (3 a-c) begins from the surface region of the compressed prepregs, and continues towards the inner part of the prepreg lay–up. As the temperature rises, the crosslinking of epoxy resin starts. Due to the addition a polymerization (of the present matrix system), no evolution of any reaction by products or solvent occurs during compositor fabrication, and this reduces the void content of the prepared composites and provides good mechanical strength (Table 3).

CONCLUSION

Produced unsaturated polyester-s-triazine has good thermal stability, ease of processing on glass reinforcement, chemical resistivity and good mechanical properties.

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