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Material applications of novel interacting blends having S-triazine containing unsaturated Polyesters and epoxy resin residues

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Abstract: 2-(4-Methyl-1-piperazinylo)-4,6-bismaleatedethylamino-1,3,5-triazine(MBT) was prepared by reaction of 2-(4-Methyl-1-piperazinylo)-4,6-bishydroxy ethyl amino -1,3,5-triazine and maleic anhydride. The MBT derivative was characterized by elemental analysis, acid value and spectral studies.

MBT 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 were monitored on Differential Scanning Calorimeter (DSC) and based on DSC data the glass reinforced composites (GRCs) were prepared and characterized by physical, chemical and mechanical properties.

Keywords: Unsaturated polyester-s-triazine (UPETs), maleic anhydride, epoxy resins (DGEBA, DGEBF, DGEBC), DSC, TGA, glass reinforced composites (GRC).

Introduction

Number of derivatives containing s-triazine ring have been reported as heterocyclic compounds [1, 2]. They are applicable mostly as reactive dyes and some are used as polymers and drugs. The aryl hydrazine derivatives containing s-triazine ring are reported by us recently [3-7]. In this context one of the present authors [RPP] reported the initial work in this direction [8]. In continuous of this work [8] 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

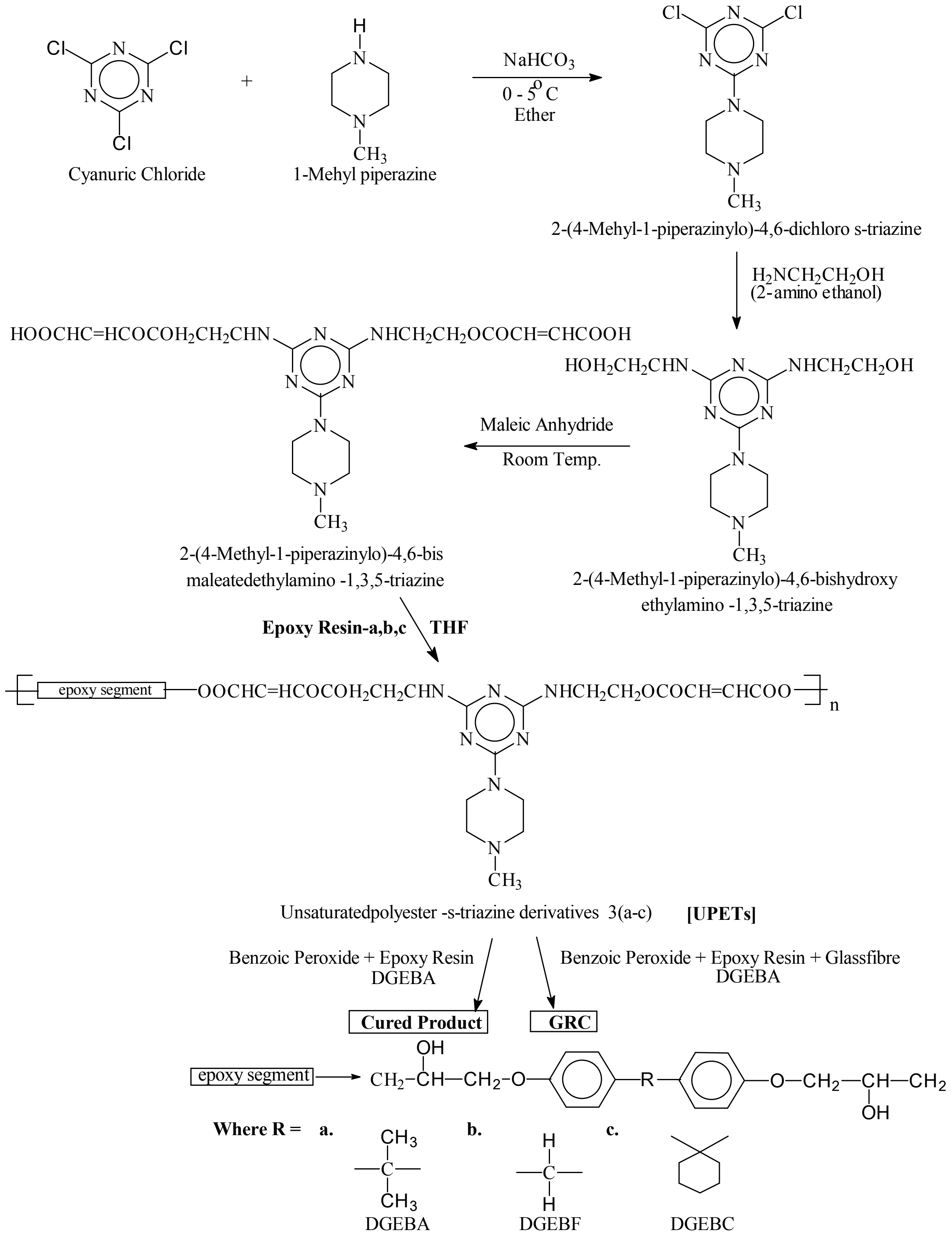

Figure-1 Preparation of UPETs

Experimental

Materials

(1) Cyanuric chloride, maleic anhydride and amino ethanol were obtained as Analar grade from local dealer. 2-(4-Methyl-1-piperazinylo)–4, 6-dichloro–1, 3, 5-triazine was prepared by reported method [8]. All other chemicals used were of laboratory grade.

(2) Epoxy resins namely diglycidyl ether of bisphenol-A (DGEBA) and diglycidyl ether of bisphenol-F (DGEBF) were obtained from local market and diglycidyl ether of bisphenol-C (DGEBC) was prepared in laboratory as per method of DGEBA [9]. Specifications of epoxy resin are as follows:

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

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

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

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

Procedures

1.Synthesis of 2(4-Methyl-1-piperazinylo)-4, 6-bishydroxyethylamino–1, 3, 5-triazines (PHS):

To a well stirred solution of 2-(4-Methyl-1-piperazinylo)–4, 6-dichloro–1, 3, 5-triazine (0.01 mole) in tetrahydrofuran (THF) solvent (50ml), a solution of amino ethanol (0.02mole) in THF (50ml) was added gradually at room temperature. The mixture was stirred for two hours. Then the mixture was refluxed for further two hours. The resultant solid product was filtered, washed with THF and air-dried. FTIR(KBr,$\nu_{max,}$cm^{-1}): 3200 – 3600 cm^{-1} (OH,s), 3400 cm^{-1} (NH,s), 3030, 1500, 1600 cm^{-1} (Ar, w), 2950, 1370 cm^{-1} ($CH_{3,}$m), 1510, 1250, 870 cm^{-1},(s-triazine, s),NH hump not visible,^{1}H NMR data(CDCI$_3$), δ 3.65(s,2H,-OH), 3.5(t,4H,-CH_2OH),2.5-2.8(t,4H,-$NHCH_2$), 1.7(s,3H,CH_3),3.1-3.4(t,8H,NCH_2CH_2N), M.F:$C_{12}H_{23}N_7O_2$, M.W:297gm,

Found C,48.03;H,7.70;N,32.87%,Anal Caled for C 48.48;H 7.74;N,32.99%.

2.Synthesis of 2-(4-Methyl-1-piperazinylo)-4, 6-bismaleatedethylamino-1, 3, 5-triazine (MBT) :

To a well stirred solution of 2(4-Methyl-1Piperazinylo)-4, 6- bishydroxy ethyl amino–1,3,5-triazine and maleic anhydride (0.02 mole) was added at room temperature. Few drops of pyridine were added and the mixture was refluxed for 6hrs. The resultant mixture was poured into water. The ppts were collected, washed and air dried. It was solid amorphous powder M.P. 211-12^{0}C (uncorrected). FTIR(KBr,$\nu_{max,}$cm^{-1}): 1680 cm^{-1} (COOH,s), 3400 cm^{-1} (NH,s), 3030, 1500, 1600 cm^{-1} (Ar, w), 2950, 1370 cm^{-1} ($CH_{3,}$m), 1510, 1250, 870 cm^{-1},(s-triazine, s),NH hump not visible, 1700 cm^{-1}(esters), ^{1}H NMR data (CDCI$_3$),δ3.5(t,4H,-CH_2OH),2.5-2.8(t,4H,-$NHCH_2$),1.7(s,3H,CH_3),3.1-3.4(t,8H,NCH_2CH_2N), 6.3(s,2H,COCH), 6.5(s,2H,CHCOOH),11.2(s,2H,COOH), M.F:$C_{20}H_{27}N_7O_8$, M.W:493gm,

Found C,48.50;H,5.30;N, 19.67%,Anal Caled for C,48.68;H,5.47;N,19.87% Acid Value :Theoretical : 227.1mg KOH/1g. sample, Found: 225.9 mg KOH/1g. sample.

3.Synthesis of unsaturated polyester -s-triazine derivatives 3(a-c) [UPETs]:

Epoxy resin (DGEBA, DGEBF and DGEBC) (1.0mole) and 2-(4-Methyl-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, 1ml trimethylamine (TEA) was added as a catalyst. The resulting mixture was slowly heated up to 85^{0}C along with continuous stirring. All the three resins were obtained in the form of 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 was determined by TF flash EA 1101. The FT-IR spectra of (3a-c) compounds were scanned in KBr pallets on Perkin Elmer FT-IR spectrophotometer [10-12]. The NMR spectra were scanned on Perkin Elmer FT-NMR spectrophotometer.

Composites Fabrication

A suspension mixture of DGEBA epoxy resin and UPETs (3a-c) at stoichiometric ratio suspended in tetrahydrofuran was prepared and 10mg benzoic peroxide (BPO) was added then stirred well for 2 to 5 min. The suspension was applied with a brush on to a 150 mm x 150 mm epoxy compatible fibre 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 hrs. The composites so obtained were cooled to 45°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions. The entire chemical and mechanical was conducted according to the ASTM or IS methods [13].

Mechanical Testing

All chemical resistance of the composites was measured according to the ASTM D543 method and all mechanical testing was performed using specimens and their average results 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 Differential Scanning Calorimeter (DSC). 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 (ΔH=28.45J/g). Curing was carried out from 30^0-300^0C at 10^0C 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 Thermo gravimetric analysis (TGA)[15,16] on a "PERKIN ELMER USA PYRES TGA-1" in a slow stream of air at a heating rate of 10^0C min^{-1}. The results are furnished in Table-4.

Table-1: **Characterization of unsaturated polyester-s-triazine derivatives (3a-c)**

Compound	Molecular Formula	Mol. Weight	% C		% H		% N	
			Cald.	Found	Cald	Found	Cald	Found
3a	$C_{41}H_{51}N_7O_{12}$	833	59.06	58.87	6.12	5.92	11.76	11.57
3b	$C_{39}H_{47}N_7O_{12}$	805	58.13	57.94	5.83	5.65	12.17	11.98
3c	$C_{44}H_{55}N_7O_{12}$	873	60.48	60.29	6.30	6.11	11.22	11.03

Table: 2: Mechanical and chemical properties of GRC based on $UPET_S$ (3a-c)-DGEBA epoxy resin

GRC	$UPET_S$-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	1.86	286	193	89	1.1	1.0
2.	3b	1.95	277	203	97	1.2	1.1
3	3c	1.92	244	197	115	1.1	1.1

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	117	161	168	32.07	1.09
3b	102	146	167	30.05	1.10
3c	108	154	165	30.08	0.97

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				
	200	300	400	500	600
3a	4.2	13	60	88	98
3b	4.5	14	62	89	99
3c	4.3	13	61	86	98

Results and Discussion

The reaction between maleic anhydride and 2-(4-Methyl-1-piperazinylo)-4,6-bishydroxyethylamino-1,3,5-triazine is facile. The products (3a-c) are 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 up to 150^0C. Hence the curing of $UPET_S$ was attempt with DGEBA resin. The unreinforced cured epoxy resin (3a-c) products were also analyzed thermo gravimetrically (TGA). TGA data of all the cured samples are shown in the Table-4. Examination of the TGA traces of cured samples reveals that each of them degrades in a single step. The results reveal that the cured samples start their degradation at about 200^0C 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 13% is found at 300^0C. However the rate of decomposition increases very rapidly between 300^0 to 450^0C and the products are lost completely beyond $800\text{-}850^0$C

The cross-linking of epoxy resin by various 3a-c begins from the surface region of the compressed prepreges, and continues towards the inner part of the preprege lay – up. As the temperature rises, cross – linking of epoxy resin starts. Due to the addition polymerization (of 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 mechanical properties are good.

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