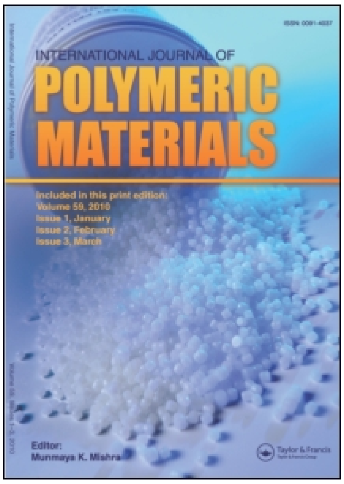

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Novel Piperazinylo Bisaryl Hydrazino-s-Triazine Derivatives and Their Application as Epoxy Resin Curing Agents

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Various 2-(4-ethyl-1-piperazinylo)-4,6-bisarylhydrazino-1,3,5-triazine (3a–f) were prepared by the reaction of 2-(4-ethyl-1-piperazinylo)-4,6-dichloro-1,3,5-triazine and various phenyl hydrazine derivatives. All the 3a–f derivatives were characterized by elemental analysis and IR spectral studies. All the 3a–f compounds were screened for microbial activity against gram-positive and gram-negative bacteria.

All these derivatives were employed as the epoxy resin curing agent. Thus the curing of the epoxy diglycidyl ether of bisphenol-A (DGEBA) was monitored by differential scanning calorimeter (DSC). Based on DSC parameters and glass-fiber reinforced composites based on DGEBA-3(a-f) systems were prepared and characterized.

Keywords: antimicrobial activity, composites, DSC, epoxy resin, hydrazines, IR and spectral study, piperazinylobisarylhydrazino-s-triazine derivatives

INTRODUCTION

The number of derivatives containing s-triazine ring have been reported as hetrocyclic compounds [1]. They are applicable mostly as reactive dyes and some are used as polymers and drugs [2,3]. The aryl hydrazine derivatives containing s-triazine ring are not reported except for one instance [4]. Recently our university scientists have studied the hydrazine triazine clubbed molecules having alkoxy group [4]. In continuation of this work [4], we report studies on phenyl hydrazine

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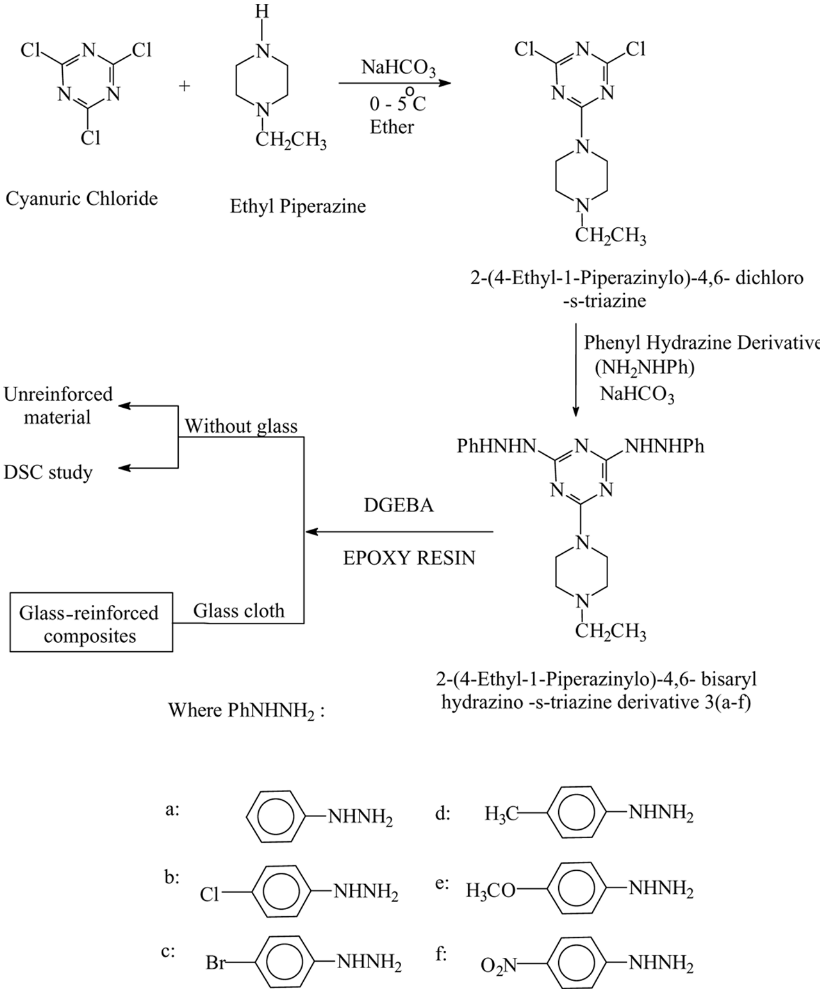


SCHEME 1 Synthesis and Application of Triazine Derivatives.

derivatives based on 2-(4-ethyl1-piperazinylo)-4,6-dichloro-1,3,5-triazine [5]. The work is descried in Scheme 1.

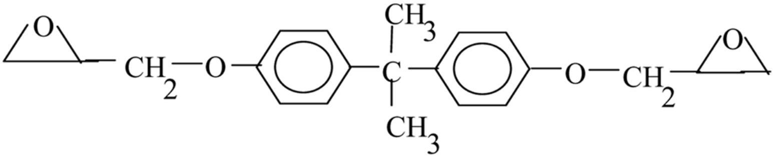
EXPERIMENTAL

Materials

1. Cyanuric chloride and all the phenyl hydrazine derivatives (substitution shown in Scheme 1) were obtained as Analar grade from local dealer.

2-(4-ethyl-1-piperazinylo)-4,6-dichloro-1,3,5-triazine was prepared by the reported method [4]. All other chemicals used were of laboratory grade.

2. Epoxy Resin Commercial epoxy resin DGEBA was obtained from the local market. Specifications of epoxy resin are as follows: Epoxy equivalent weight 190, Viscosity at 25°C 9000–11000 cps



Epoxy resin [DGEBA]

3. Glass cloth.

Synthesis of Piperazinylo Bisaryl Hydrazino-s-Triazines

2-(4-ethyl-1-piperazinylo)-4,6-bisarylhydrazino-1,3,5-triazines (3a–f). The general procedure for these compounds is as follows.

To a well-stirred solution of 2-(4-ethyl-1-piperazinylo)-4,6-dichloro-1,3,5-triazine (0.01 mol) in tetrahydrofuran (THF) solvent (50 ml) a solution of phenyl hydrazine (or substituted phenyl hydrazine) (Scheme 1) (0.02 mol) in THF (50 ml) 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. All the 3a–f compounds listed in Table 1 were dark yellow.

TABLE 1 Characterization of 2-(4-ethyl-1-piperazinylo)-4,6-bisaryl hydrazino-1,3,5-triazines (3a–f)

Compound	Molecular formula	Mol. weight	% C		% H		% N	
			Cald.	Found	Cald	Found	Cald	Found
3a	$C_{21}H_{27}N_9$	405	62.22	62.0	6.66	6.5	31.11	30.9
3b	$C_{21}H_{25}N_9Cl_2$	474	53.16	53.0	5.27	5.1	26.58	26.4
3c	$C_{21}H_{25}N_9Br_2$	563	44.76	44.6	4.44	4.3	22.38	22.2
3d	$C_{23}H_{31}N_9$	433	63.74	63.6	7.15	7.0	29.09	28.9
3e	$C_{23}H_{31}N_9O_2$	465	59.35	59.2	6.66	6.5	27.09	26.9
3f	$C_{21}H_{25}N_{11}O_4$	495	50.90	50.7	5.05	4.9	31.11	30.9

COMPOSITES FABRICATION

A suspension mixture of epoxy resin and 3a–f at stoichiometric ratio suspended in tetrahydrofuran was prepared and was stirred well for 2 to 5 min. The suspension was applied with a brush on to a 150 mm × 150 mm epoxy compatible fiberglass cloth and the solvent was allowed to evaporate. Once dried, 10 plies of prepreg thus prepared were stacked one on top of another, pressed between steel plates coated with a Teflon release film 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 composite 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.

Mechanical Testing

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

MEASUREMENTS

The elemental analysis of all 3a–f compounds was determined by TF flash EA 1101. The FTIR spectra of 3a–f compounds were scanned in KBr pallets on Perkin Elmer FTIR spectrophotometer. The NMR spectra of soluble sample No. 3e was scanned on a Perkins Elmer FT-NMR spectrophotometer.

TABLE 2 Mechanical and Electrical Properties of Composites Based on DGEBA-3a–f

Resin system	Specific gravity	Impact strength (Mpa)	Compressive strength (Mpa)	Rockwell hardness (R)	% change on exposure to 25% W/v NaOH	
					Thickness	Weight
3a	1.85	280	185	39.9	1.0	1.0
3b	1.95	270	195	39.3	1.0	1.0
3c	1.88	240	188	38.3	1.0	1.2
3d	1.91	235	191	40.2	1.2	1.3
3e	1.90	240	190	40.0	1.4	1.0
3f	1.88	230	188	39.4	1.4	1.2

Curing

Curing of DGEBA-(3a–f) was carried out on a differential scanning calorimeter (DSC). A DuPont High Pressure DSC-9900 Thermal Analyzer 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^{-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) 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.

The temperature ranges for curing of the epoxy resin 3a–f system are summarized in Table 5.

Antimicrobial Activity

For testing antimicrobial activity various microorganism Swere used. The pour plate agar method was used for this study. The following general procedure is adopted [6, 7].

The antimicrobial activity of all the compounds was studied at 1000 ppm concentration in vitro. The different types of microorganism used were some gram-negative bacteria [*Escherichia coli, Proteus valgaris*], gram-positive bacteria [*Bacillus cereus, Streptococus species*], fungi [*Aspergillus oryzac*], yeast [*Pichia species*] and actinomycetes [*Streptomyces coleicor*].

The antibacterial activity of 3a–f compounds was measured on each of these microorganism strains on a potato dextrose agar medium (PDA). Such a PDA medium contained [7] potato 200 g, dextrose

TABLE 3 DSC Curing Data of DGEBA-3a–f System

DGEBA-(3a–f) system	Curing temp. (T°C) T_i	T_p	T_f
3a	110	155	163
3b	100	142	131
3c	105	150	159
3d	108	135	165
3e	100	146	165
3f	140	114	164

TABLE 4 TGA of DGEBA-3a-f Cured Materials

	% weight loss at various temp.C°				
DGEBA-(3a-f)	200	300	400	500	600
3a	2.1	10	55	77	99
3b	2.2	9	54	79	98
3c	2.5	10	55	77	98
3d	2	9	55	76	99
3e	2.1	8	56	79	98
3f	2	9	55	80	99

20 g, agar 30 g, and water 1 l. PDA medium autoclaved at 121°C and 15 lbs pressure for 15 min. After autoclaving, the compounds to be tested were inoculated (1000 ppm) in PDA medium at 42°C temperature and mixed than these media were poured into sterile empty glass petriiplates. The tested microorganism [young culture] were inoculated after solidification of the PDA medium plates. The percentage inhibition of growth of microorganism was calculated after 5 days of incubation at appropriate temperature [bacteria- 37°C, fungi- 25°C, Actinomyces- room temp.] percentage of inhibition of microorganism was calculated by using the formula given below.

$$\text{Percentage of inhibition of growth of microorganism} = \frac{100(X - Y)}{X}$$

where, X = area of bacterial growth in control plate (mm),
Y = area of bacterial growth in test plate (mm).

The antimicrobial activity of all the 3a–f compounds are furnished in Table 6.

TABLE 5 Curing Characteristic of DGEBA-3a–f System (1:1) at 10°C/min

DGEBA-(3a–f)	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	115	155	163	32.08	1.10
3b	99	142	161	29.12	1.12
3c	105	150	159	30.32	0.90
3d	108	135	165	33.10	1.10
3e	100	146	165	34.50	0.82
3f	140	114	164	39.30	1.11

TABLE 6 Antimicrobial activity of 2-(4-ethyl-1-piperazinylo)-4,6-bisaryl hydrazino-1,3,5-triazines

	Percentage of inhibition of growth at 1000 ppm (%) concentrate of sample						
Sample	*Bacillus cereus*	*Streptococcus species*	*Escherichia coli*	*Proteusvul garis*	*Aspergills oryzac*	*Pichia species*	*Streptomyces coleicolr*
Control	NIL	NIL	NIL	NIL	NIL	NIL	NIL
3a	66	95	81	81	65	67	60
3b	100	96	96	96	98	98	95
3c	72	92	100	78	64	72	60
3d	73	86	71	57	64	67	60
3e	85	83	94	69	60	68	65
3f	67	66	99	61	66	65	59

RESULTS AND DISCUSSION

The reaction between phenyl hydrazine and 2-(4-ethyl-1-piperazinylo)-4,6-bisaryl hydrazino-1,3,5-triazines is facile. The products (3a–f) are dark yellow amorphous powders. The C, H, N contents of all (3a–f) shown in Table 1 are consistent with the predicated structures shown in Scheme 1. The IR spectra of all 3a–f are almost identical. All the IR spectra comprise the following important features.

1. –NH–NH– (hydrazine group): 3280, 1610, 820 cm^{-1}
2. s-triazine: 1510, 1250, 870 cm^{-1}
3. CH_2: 2920, 2830, 1450 cm^{-1}
4. Aromatic: 3030, 1500, 1600 cm^{-1}

As the compounds 3a–f except 3e are insoluble in $CDCl_3$, an NMR spectral study was attempted for 3e. The NMR spectrum of 3e comprises the multiplate between 6.9 to 8.1 δ ppm mainly due to aromatic protons, while the signal at 2.6 δ ppm with integration of 6H is responsible for two CH_3 of OCH_3 groups. The signals in most downfield (9.5 δ ppm) is from NH–NH protons. The result of antimicrobial screening showed (Table 6) that compounds 3b,c,f displayed a high order of antibacterial activity and remaining compounds showed weak to moderate activity against both the bacteria. Similarly compounds 3a, d, and e showed higher antifungal activity and remaining compounds displayed moderate antifungal activity against both the fungi.

The structure of the glass cloth cores fibres in the direction of core-plane is almost random. There are relatively few fibers oriented in the direction perpendicular to the plane. During compression, the fiber structure oriented perpendicular to the plane is diminished during compression. The unreinforced cured DGEBA-(3a-f) 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. However the rate of decomposition increases very rapidly between 300 to 450°C and the products are lost completely beyond 850°C.

The crosslinking of epoxy resin by various 3a–f begins from the surface region of the compressed prepregs, and continues towards the inner part of the prepreg lay – up. As the temperature rises, crosslinking of epoxy resin starts. Due to the addition polymerization (of the present matrix system), no evolution of any reaction by–products or solvent occurs during composite fabrication and this reduces the void content of the prepared composites and provides good mechanical strength (Table 2).

CONCLUSION

The synthesis of 2-(4-ethyl-1-piperazinylo)-4,6-bisarylhydrazino-1,3,5-triazines is facile. The produced compounds have good microbial toxicity. Due to NH–NH groups these compounds can be utilized as an epoxy resin hardener.

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