

Synthesis, Characterization, Composites Fabrication and Antimicrobial Activity of Piperazinylo bisarylhydrazino-s-Triazine Derivatives

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Abstract : Various 2-(4-Methyl-1-Piperazinylo)-4,6-bisarylhydrazino-1,3,5-triazine(3a-f) were prepared by reaction of 2-(4-Methyl-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 antimicrobial activity against gram-positive and gram-negative bacteria.

All these derivatives were employed as epoxy resin curing agent. Thus the curing of commercial epoxy resin namely diglycidyl ether of bisphenol-F (DGEBF) was monitored on Differential Scanning Calorimeter (DSC) and thermo gravimetric analysis (TGA). Based on DSC parameters, the glass-fibre reinforced composites based on DGEBF-(3a-f) systems were prepared and characterized by physical and mechanical data

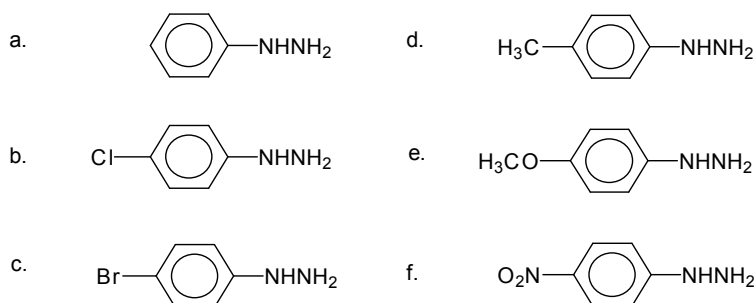
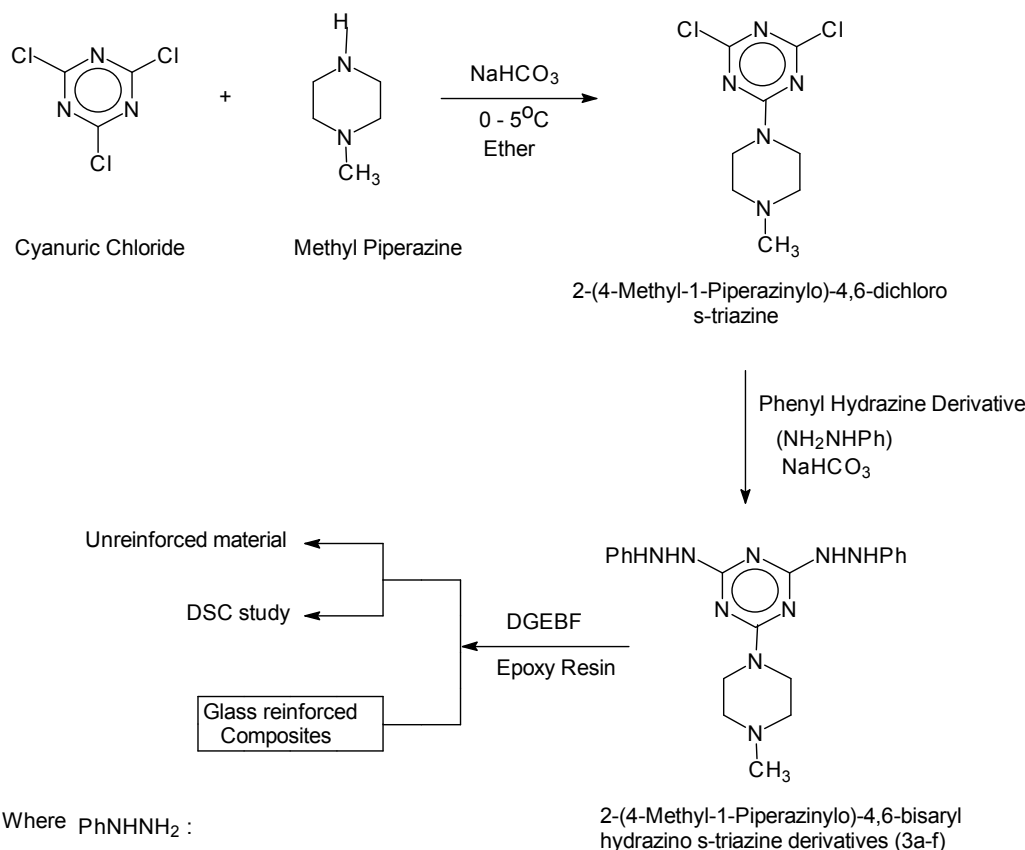
Keywords : Piperazinylo bisaryl hydrazino s-triazine derivatives, hydrazines, IR & spectral study, antimicrobial activity, epoxy resin (DGEBF), DSC, TGA, glass reinforced composites (GRC).

Introduction

Number of derivatives containing s-triazine ring have been reported as hetrocyclic compounds [1-3]. They are applicable mostly as reactive dyes and some are used as polymers and drugs [4]. The aryl hydrazine derivatives containing s-triazine ring are not reported so far except one instance. Now in this

context we recently [5-7] reported the such derivative curing ethyl piperazing-s-triazine as DGEBA epoxy resin curing agent in continuous of this work [8]. We reported the studies on the phenyl hydrazine derivatives of based on 2-(4-Methyl 1-Piperazinylo)-4,6-dichloro-1,3,5-triazine. The work is designed in scheme-1.

Scheme-1

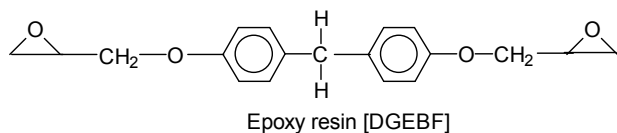


Experimental

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-Methyl-1-Piperazinylo)-4,6-dichloro-1,3,5-triazine was prepared by reported method [10]. All other chemicals used were obtained of laboratory grade.

(2) Epoxy Resin Commercial epoxy resin DGEBF [9] was obtained from local market. Specifications of epoxy resin are as follows: Epoxy equivalent weight 175, Viscosity at 25°C 15000-17000 cps.



(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.m² were used for composite fabrication.

Synthesis of Piperazinylo bisaryl hydrazino-s-triazines

2-(4-Methyl-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-Methyl-1-Piperazinylo)-4,6-dichloro-1,3,5-triazine (0.01 mole) in tetra hydro furan (THF) solvent (50ml) a solution of phenyl hydrazine (or substituted phenyl hydrazine) (scheme-1) (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. All the (3a-f) compounds listed in Table-1 were dark yellow amorphous powders.

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 x 150 mm epoxy compatible fibre glass cloth and the solvent was allowed to evaporate. Once dried, the 10 plies of prepegs 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 prepegS stack was cured by heating in the press to 120-140⁰C for 12 hrs. The composites so obtained was cooled to 45⁰C 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 test were conducted according to the ASTM or IS methods.

Mechanical Testing

All mechanical testing was performed using six test specimens and their average results in Table-2. The compressive strength was measured according to the IS method [10] at room temperature.

Mesurements

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

Curing

Curing of DGEBF-3a-f was carried out [11] on a Differential Scanning Calorimeter (DSC) [12]. A Du Point High Pressure DSC-9900 Thermal Analyzer was used for this study. The instrument was calibrated using standard indium metals with known heats of fusion ($\Delta H=28.45\text{J/g}$). curing was carried out from 30⁰-300⁰C at 10⁰C 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) [13,14] on a "PERKIN ELMER USA PYRES TGA-1" in a slow stream of air at a heating rate of 10⁰C min⁻¹. The results are furnished in Table-4.

The curing reaction of epoxy resin and 3a-f studied of for stoichiometric ratio of epoxy resin-3a-f.

Antimicrobial Activity

For the testing antimicrobial activity various microorganism were used for the study. The pour plate agar method was used for this study. Following general procedure is adopted [15,16].

The antimicrobial activity of all the compounds was studies at 1000 ppm concentration in vitro. The different types of microorganism used were some gram negative bacteria [*Escherichia coli*, *Proteus vulgaris*], gram positive bacteria [*Bacillus cereus*, *Streptococcus species*], fungi [*Aspergillus oryzae*], 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 potato 200gram, dextrose 20gram, agar 30gram, and water 1 Litre. PDA medium autoclaved at 121⁰C temperature and 15 lbs pressure for 15 minute. After autoclaving the compounds to be tested were inoculated (1000 ppm) in PDA medium at 42⁰C temperature and mix it than these media were poured in to sterile empty glass petriplates. The testing microorganism [young culture] were inoculating after solidification of the PDA medium plates. The percentage inhibition of growth of microorganism was calculated after 5 days of incubation of PDA medium plate inoculated with microorganism at appropriate temperature [*Bacteria*- 37⁰C, *Fungi*- 25⁰C, *Actinomyces*- room temp.] percentage of inhibition of microorganism was calculated by using the formula given below.

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

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-5

Table-1: Characterization of 2-(4-Methyl-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 ₂₀ H ₂₅ N ₉ | 391 | 61.38 | 61.25 | 6.39 | 6.25 | 32.22 | 32.10 |
| 3b | C ₂₀ H ₂₃ N ₉ Cl ₂ | 460 | 52.17 | 52.00 | 5.00 | 4.85 | 27.39 | 27.25 |
| 3c | C ₂₀ H ₂₃ N ₉ Br ₂ | 549 | 43.72 | 43.60 | 4.19 | 4.05 | 22.95 | 22.80 |
| 3d | C ₂₂ H ₂₉ N ₉ | 419 | 63.00 | 62.85 | 6.92 | 6.75 | 30.07 | 29.90 |
| 3e | C ₂₂ H ₂₉ N ₉ O ₂ | 451 | 58.54 | 58.40 | 6.43 | 6.30 | 27.93 | 27.75 |
| 3f | C ₂₀ H ₂₃ N ₁₁ O ₄ | 481 | 49.84 | 49.70 | 4.78 | 4.65 | 32.01 | 31.85 |

Table-2: Mechanical and electrical properties of composites based on DGEBF-(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 | 283 | 195 | 100 | 1.2 | 1.0 |
| 3b | 1.90 | 273 | 205 | 102 | 1.1 | 1.1 |
| 3c | 1.88 | 243 | 198 | 104 | 1.0 | 1.2 |
| 3d | 1.90 | 238 | 199 | 106 | 1.2 | 1.2 |
| 3e | 1.90 | 243 | 199 | 110 | 1.3 | 1.0 |
| 3f | 1.85 | 233 | 198 | 108 | 1.2 | 1.0 |

Table -3: Curing characteristic

| DGEBF-3(a-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 | 117 | 158 | 166 | 33.08 | 1.10 |
| 3b | 101 | 145 | 164 | 31.10 | 1.12 |
| 3c | 105 | 153 | 162 | 32.32 | 0.95 |
| 3d | 110 | 138 | 168 | 35.10 | 1.10 |
| 3e | 102 | 149 | 168 | 36.55 | 0.86 |
| 3f | 142 | 117 | 168 | 40.38 | 1.11 |

Table-4: TGA of DGEBF-(3a-f) cured materials DGEBF-3(a to f) system (1 : 1) at 10 ° C / min.

| DGEBF-(3a-f) | % weight loss at various temp.C ⁰ | | | | |
|--------------|--|------|-----|-----|-----|
| | 200 | 300 | 400 | 500 | 600 |
| 3a | 2.0 | 10.3 | 57 | 79 | 98 |
| 3b | 2.2 | 9.3 | 56 | 80 | 99 |
| 3c | 2.3 | 10.2 | 55 | 81 | 99 |
| 3d | 2.4 | 9.4 | 56 | 79 | 99 |
| 3e | 2.1 | 8.1 | 57 | 79 | 98 |
| 3f | 2.0 | 9.2 | 58 | 82 | 98 |

Table- 5: Antimicrobial activity of 2 –(4-Methyl-1-piperazinylo)-4,6- bisaryl hydrazino –1,3,5- triazines

| Sample | Percentage of inhibition of growth at 1000 ppm (%) concentrate of sample | | | | | | |
|---------|--|-------------------------------|-------------------------|-------------------------|---------------------------|-----------------------|---------------------------------|
| | <i>Bacillus cereus</i> | <i>Strepto-coccus species</i> | <i>Escherichi-acoli</i> | <i>Proteus-vulgaris</i> | <i>Aspergillus oryzac</i> | <i>Pichia species</i> | <i>Strepto-myces coleicolor</i> |
| Control | NIL | NIL | NIL | NIL | NIL | NIL | NIL |
| 3-a | 62 | 92 | 77 | 77 | 62 | 66 | 58 |
| 3-b | 98 | 95 | 94 | 93 | 97 | 95 | 94 |
| 3-c | 68 | 88 | 98 | 75 | 63 | 69 | 58 |
| 3-d | 70 | 82 | 70 | 53 | 60 | 66 | 58 |
| 3-e | 85 | 82 | 92 | 65 | 58 | 66 | 62 |
| 3-f | 66 | 66 | 96 | 60 | 62 | 64 | 56 |

Results and discussion

The reaction between phenyl hydrazine and 2 –(4-Methyl-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 [17-19] of all (3a-f) are almost identical. All the IR spectra comprises 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}
5. CH_3 : 2950, 1370 cm^{-1}

As the compounds (3a-f) except 3e are insoluble in CDCl_3 , the NMR spectral study 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-5) 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 fibres oriented in the direction perpendicular to the plane. During compression, the fibre structure oriented perpendicular to the plane is diminished during compression.

The unreinforced cured DGEBF-(3a-f) products were also analyzed thermo gravimetrically (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 $^{\circ}\text{C}$ 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 $^{\circ}$. However the rate of decomposition increases very rapidly between 300 $^{\circ}$ to 450 $^{\circ}\text{C}$ and the products are lost completely beyond 850 $^{\circ}\text{C}$.

The cross-linking of epoxy resin by various 3a-f begins from the surface region of the compressed prepegs, and continues towards the inner part of the prepegs 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 compositer fabrication and this reduces the void content of the prepared composites and provides good mechanical strength (Table-2).

Conclusion:

The synthesis of 2–(4-Methyl-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 for epoxy resin hardner. Such work in polymer journal will be published shortly.

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