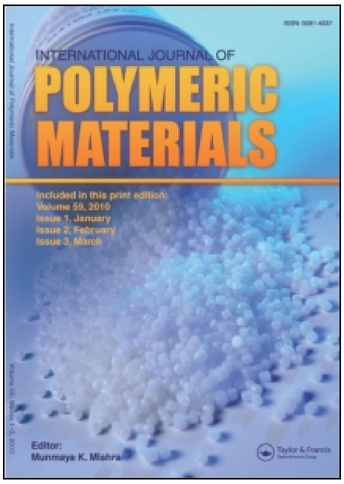

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Synthesis and Characterization of Chromophoric Polyureas

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Crysodine type dyes were prepared by the coupling of 2-diazobenzothiazole derivatives with 1,3-benzenediamine. The resultant dyes were characterized duly. Each dye was then polycondensed with 1,6-hexamethylene diisocyanate. The resultant polyureas (PU) having a pendent azo chromophoric group were characterized by elemental analysis, spectral studies, and number average molecular weight ($\overline{Mn}$) estimated by nonaqueous conductometric titration and thermogravimetry.

A commercial diglycidylether of bisphenol-A (DGEBA) epoxy resin was cured by using these PUs. The study was monitored by differential scanning calorimetry (DSC) and glass reinforcement.

Keywords differential scanning calorimeter (DSC), epoxy resin, glass-reinforced composites, infrared spectra (IR), number average molecular weight ($\overline{Mn}$), polyureas, thermogravimetry analysis (TGA)

INTRODUCTION

Polyureas may be classified as heterochain macromolecules, which contain urea groups in their chain. Although the chemistry and technology of polyureas are of recent origin, the chemistry of ureas dates back over 100 years. Linear polyureas are thermoplastic polycondensation products with aliphatic

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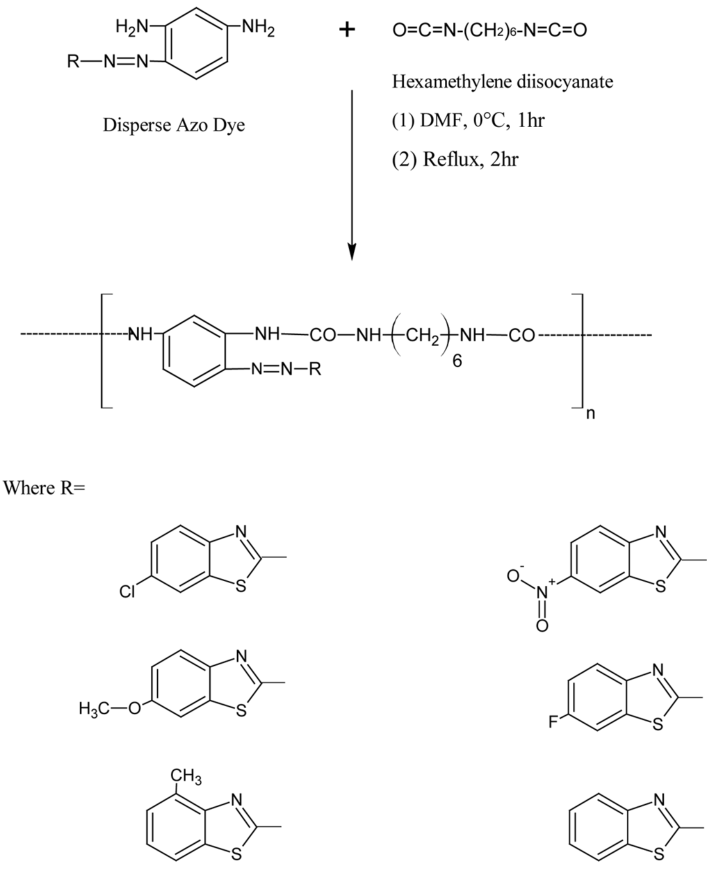
or aromatic structures. Polyureas or copolyureas containing aliphatic structures exhibit a difference of 50–100°C between melting points and the beginning of decomposition; they are used for castings. Polyureas containing aromatic structures melt near their decomposition temperatures. They are soluble in some organic solvents and can be used for preparation of lacquers, varnishes and coatings [1]. Polyureas were first prepared on a commercial scale at I.G. Farben, employing the reaction between diisocyanate and diamines. Mitsui Toatsu Chemical Ltd. produces synthetic fibers from nonamethylenediamine and urea. Today, polyureas and copolyureas (especially poly (urethane-ureas) have many practical applications as foams, elastomers, adhesives, and fibers [2].

The area of colored polyureas has not received attention academically even though they contain a number of diamine groups (i.e., capable for reaction with diisocyanate). Hence, the initial work in this respect has been reported by Indian authors [3–5]. In continuation of this work, the present paper



Scheme 1: Synthesis steps.

comprises synthesis, characterization and electrical conductivity of polyureas (PUs) containing azobenzothiazole (a heteroaryl) as pendent moiety. The PUs-DGEBA (a commercial epoxy resin) curing system was monitored by DSC. Based on DSC thermograms, glass-reinforced composites have been laminated and characterized by chemical, mechanical and electrical properties. The whole synthetic route is shown in Scheme 1.

EXPERIMENTAL

Materials

Diglycidylether of bisphenol-A (DGEBA) and E-type glass-woven fabric (0.25 mm thick) were obtained from Unnati Chemicals, India. All other chemicals used were of analytical grade. Various 2-aminobenzothiazoles were prepared by the methods reported in the literature [6].

Synthesis of Azo Disperse Dyes

The azo disperse dyes having the structures shown in Scheme 1 were prepared by the method reported in the literature [7].

Synthesis of Colored Polyureas (PUs)

All the polyureas based on azo disperse dyes were prepared in a similar manner. The general process is as follows:

To an ice-cooled solution of azo disperse dye sample (0.01 moles) in dry N,N′-dimethylformamide (50 ml) a solution of hexamethylene diisocyanate (0.01 mole) in 50 ml dry N,N′-dimethylformamide was added gradually with constant stirring. The colloidal suspension which formed immediately was then stirred at room temperature for an hour. The resultant suspension was refluxed for 2 h. The resulting solid product was then filtered off and air-dried (95% yields).

Synthesis of PU-Epoxy Resin Curing Systems

A PU-epoxy resin system has been prepared by mixing PU and epoxy resin (DGEBA) at stoichiometric ratio. The mixture was stirred well for 15 min to form a homogeneous system.

Composite Fabrication

Suspension of PU-epoxy resin (DGEBA) (PUER) systems were prepared in tetrahydrofuran (THF) and stirred well for 10 min. The suspension was applied with a brush to 250 mm × 250 mm phenolic-compatible fiberglass cloth and the solvent was allowed to evaporate. The dried ten prepregs so prepared were stacked one over another and pressed between steel plates coated with a Teflon film release sheet and compressed in a flat platen press under 70 psi pressure. The prepreg stacks were cured by heating at $175 \pm 10^\circ C$ for 4 h in an air-circulated oven. The composite so obtained was cooled to 50°C before the pressure was released.

ANALYSIS AND CURING STUDY

The C, H, and N contents were estimated by means of Thermofinigen-1101 Flash elemental analyzer (Italy). The sulfur content was determined by Carius method [8]. The IR spectra of all the polymers were scanned in KBr pellets on a Perkin Elmer 257 spectrophotometer. The number average molecular weights ($\overline{Mn}$) of PUs were estimated by nonaqueous conductometric titration. The titration was carried out in formic acid against perchloric acid as titrant. A digital conductometer, Toshniwal, India, was used for this purpose. The values of the number average molecular weight ($\overline{Mn}$) of all polymer samples were calculated following the method reported in the literature [9]. Thermogravimetric analysis for polymers was carried out on Du Pont thermobalance in air at a heating rate of $10^\circ K\ min^{-1}$. The electrical conductivity of each sample was measured on pellets (1 cm diameter, 0.45 cm thickness) at room temperature using a Million Megohmmeter RM 160 MK IIA BPL, India. The preparations of the pellets of all the PU samples and other details have been described in an earlier communication [10].

Curing

A Du Pont 900 DSC was used for the curing study of PU-epoxy resin (PUER) curing systems. The instrument was calibrated using standard indium metal with known heat of fusion ($\Delta H = 28.45\ J/g$). Curing was carried out using a single heating rate of 10°C/min in air. The sample weight for this investigation was in the range of 4–5 mg along with an empty reference cell.

COMPOSITE CHARACTERIZATION

All the chemical, mechanical and electrical tests on composites were conducted according to the ASTM methods listed below using five specimens for each test.

Chemical Resistance Test

ASTM D 543-67 was used to measure the chemical resistance of the composites towards sodium hydroxide, organic solvents and mineral acids.

Mechanical and Electrical Testing

1. The flexural strength was measured according to ASTM D 790.
2. The compressive strength was measured according to ASTM D 695.
3. The impact strength was measured according to ASTM D 256.
4. The Rockwell hardness was measured according to ASTM D 785.
5. The electrical strength was measured according to ASTM D 149.

RESULTS AND DISCUSSION

The polyureas (PUs) formation was performed by facile reaction of $-NH_2$ group's moiety with −NCO groups. All PUs were found to be colored powders. They do not melt up to 250°C and are insoluble in common organic solvents. C, H, N, S (Table 1) of each of the PUs are consistent with the corresponding predicted structure (see Scheme 1.)

IR spectra of all the PUs are identical in almost all aspects and inspection of all the spectra reveals that the spectra comprise important IR spectral features of urea linkages. The IR bands at $1620–1680\,cm^{-1}$, and $1240–1250\,cm^{-1}$ may be due to urea linkage. The other IR spectra features are due to aromatic and aliphatic segments of monomers and appear at their expected positions.

As the produced polymers are insoluble in organic solvents, the colligative properties (i.e., viscosity, osmometry) have not been studied and hence the number average molecular weight ($\overline{Mn}$) of all the polymer samples have been measured by end group $-NH_2$ by non-aqueous conductometric titration. The results of $\overline{Mn}$ values are furnished in Table 1.

The electrical conductivities measured at room temperature of all PUs samples are shown in Table 2 and are in the range of 1.4×10^{-10} to $3.1 \times 10^{-7}\,\Omega cm^{-1}$ depending upon the nature of polymer. An examination of the results reveals that the produced PUs can be ranked as poor insulators.

TG data of PUs and PUERs are shown in Tables 3 and 4. Inspection of the TG thermograms reveals that all the PUs and PUERs decomposed in one step. They start their degradation about 200°C, and lose their weight rapidly between 200 to 600°C.

The curing study of the PU-epoxy resin (PUER) cured product was carried out on DSC. The data obtained from DSC thermograms show that all the cured PU-epoxy resin (PUER) systems give a single exothermic peak in the range of 167 to 196°C. The values of activation energy (Ea) for such system, shown in Table 5, did not vary widely. The results of curing temperature with activation energy (Ea) and order of reaction (n) are furnished in Table 5.

Table 1: Characterization of polyureas (PUs).

					Elemental analysis							
					%C		%H		%N		%S	
PU sample	Color of sample	Mole formula of repeating unit	Mol. wt. of repeating unit	$\overline{Mn}$	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
PU-1	Brown	$C_{21}H_{22}ClN_7O_2S$	473	3784	53.28	53.10	4.65	4.50	20.72	20.60	6.77	6.50
PU-2	Dark Brown	$C_{22}H_{25}N_7O_3S$	469	4690	56.29	56.20	5.33	5.30	20.90	20.70	6.82	6.80
PU-3	Reddish Brown	$C_{22}H_{25}N_7O_2S$	453	4530	58.28	58.10	5.52	5.40	21.63	21.60	7.06	6.80
PU-4	Dark Brown	$C_{21}H_{22}N_8O_4S$	484	3388	52.07	52.00	4.55	4.50	23.14	23.10	6.61	6.30
PU-5	Brown	$C_{21}H_{22}FN_7O_2S$	457	3656	55.14	55.00	4.81	4.60	21.44	21.30	7.00	6.90
PU-6	Reddish Brown	$C_{21}H_{23}N_7O_2S$	439	3942	57.40	57.30	5.24	5.20	22.32	22.30	7.29	7.00

Table 2: Electrical conductivity of PUs.

PU samples	**Electrical conductivity (σ) at 303°K (Ω.cm^{-1})**
PU-1	2.3×10^{-8}
PU-2	1.4×10^{-10}
PU-3	8.3×10^{-9}
PU-4	3.1×10^{-7}
PU-5	7.5×10^{-7}
PU-6	5.2×10^{-9}

Table 3: TGA of PUs.

	% wt. loss at various temperature °C from TGA					
PU samples	**200**	**300**	**400**	**500**	**600**	**700**
PU-1	2.1	6.9	22.6	65.2	75.9	77.3
PU-2	2.5	7.9	20.1	67.6	74.2	78.8
PU-3	2.9	8.1	21.3	68.1	74.8	79.5
PU-4	2.0	7.7	24.6	63.9	75.1	76.9
PU-5	2.7	8.3	21.6	68.2	76.2	78.6
PU-6	2.8	7.6	23.8	64.8	75.6	78.1

Table 4: TGA of unreinforced cured PU: epoxy resins (PUER) systems.

	% wt. loss at various temperature °C from TGA					
PU samples	**200**	**300**	**400**	**500**	**600**	**700**
PUER-1	1.9	6.9	16.2	49.6	53.2	57.7
PUER-2	2.1	7.8	17.2	50.3	56.5	58.6
PUER-3	2.9	8.9	17.8	51.9	54.7	56.8
PUER-4	2.4	8.8	18.4	50.2	54.2	54.3
PUER-5	2.2	9.1	18.2	51.3	58.4	60.1
PUER-6	2.0	7.5	17.3	50.9	54.0	55.4

Table 5: Curing characterization of PU: epoxy resins (PUER) systems.

PU samples	**Kick off temp. ti (°C)**	**Peak temp. tp (°C)**	**Final temp. tf (°C)**	**Activation energy (Ea) KJ/mol**	**Order of reaction 'n'**
PUER-1	147	172	192	196.6	1.9
PUER-2	151	169	197	194.7	2.0
PUER-3	150	168	199	191.1	2.1
PUER-4	149	175	200	189.6	1.8
PUER-5	155	176	207	195.3	2.0
PUER-6	146	166	190	188.1	1.9

Table 6: Chemical, mechanical and electrical properties of glass fiber-reinforced composites prepared from PU: epoxy resins (PUER) systems.

Glass fiber-reinforced composites	% Change on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
PUER-1	1.18	1.20	1.34	316	318	316	132	18.3
PUER-2	1.14	1.17	1.33	310	312	314	130	18.1
PUER-3	1.11	1.14	1.31	315	314	317	131	18.2
PUER-4	1.16	1.18	1.33	307	306	310	128	17.8
PUER-5	1.19	1.21	1.32	321	319	320	135	18.4
PUER-6	1.17	1.18	1.34	326	322	324	139	18.5

The glass-reinforced composites based on PU-epoxy resin (PUER) systems were prepared at 175 ± 10°C for 4 h. The density of all the composites was in the range of 1.31 to 1.34 g/cm^3 (shown in Table 6). Chemical resistance tests revealed that all composites had remarkable resistance properties towards organic solvents and concentrated acids (25% V/V). However, the concentrated alkali (25% W/V) caused changes in their thickness (1.11 to 1.19%) and a weight loss of about 1.14 to 1.21% was found. Electrical strength of all the composites was found in the range of 17.8 to 18.5 kV/mm. The results of composite characterizations, in Table 6, suggest that composites have good chemical, mechanical and electrical properties.

CONCLUSION

The present work deals with colored polyureas. The nature of these polymers is amorphous colored powders with good thermal stability. Having urea groups they are thermoplastic and can easily form colored articles when processed at a high temperature. The glass-reinforced composites of PU-epoxy resins (i.e., DGEBA) (PUER) systems have good chemical, mechanical, and electrical properties.

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