



Synthesis and Characterization of Glass Reinforced Composites from Polyurethanes/Epoxy Resin

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Abstract : Polyurethanes (PUTs) were prepared by the polycondensation reaction of Disperse Dyes containing Polyols and Hexamethylene diisocyanate (HMDI). All the PUTs were characterized by elemental analysis, spectral studies, end group determination and thermogravimetry. Further reaction of PUTs was carried out with an epoxy resin (i.e. DGEBA). The curing study of prepared resins was monitored by DSC. All the glass fiber reinforced composites have been laminated and characterized by chemical, mechanical and electrical properties. The unreinforced cured resins were subjected to thermogravimetric analysis (TGA).

Key words : Polyurethane, epoxy resin (DGEBA), number average molecular weight, thermogravimetry, Differential Scanning Calorimetry (DSC), Composite.

Introduction

Epoxy resins are considered as one of the most important classes of thermosetting polymers and are extensively used for their many good properties, such as high strength and stiffness, excellent chemical corrosion resistance and electrically insulating properties. Epoxy-based materials are being applied as matrix resins of coatings, adhesives and composites. However, their highly cross-linked structure results in significant brittleness. In order to circumvent this toughness problem, impact modifiers are added to epoxy resin in order to produce multiphase blends with improving toughness/stiffness balance. The experiments indicated that blending Polymers with epoxy is an effective toughening method and besides impact strength, other mechanical properties, like tensile strength and tensile modulus as well as glass transition temperature of epoxy can also be improved [1-7]. Extensive research has thus been conducted to toughen epoxy [8-9]. The block copolymers were used as effective particles to toughen brittle polymers with little loss in stiffness. This strategy was first proposed by Hillmyer et al. [10] followed by numerous other studies. Polyurethane is a versatile polymeric

material with desirable properties, such as high abrasion resistance, tear strength, excellent shock absorption, flexibility, and elasticity. The molecular structure of polyurethane (PU) is composed of urethane compounds (-NHCOO). General speaking, the block copolymer PU comprises rigid diisocyanate, short-chain diol or diamine, and polyol. Because it is resistant to chemicals, soft, waterproof, and weatherproof, it can be used for different purposes [11]. Polyurethanes have potential array of commercial applications as they can be moulded, injected, extruded and recycled. They are used in almost every industrial as well as biomedical application. Polyurethanes are block copolymers with alternating soft and hard blocks or segments [12-14]. So, the composite prepared by the combining the both properties of Epoxy Resin and Polyurethane have improved mechanical properties.

In our previous studies [15-19], we described the synthesis of polyureas from Diamines containing 2-aminobenzothiazole moiety and Hexamethylene diisocyanate and used them to modify epoxy resin, mechanical properties, and dynamic thermal mechanical properties of PU-Epoxy Resin composite. Hence, the present article comprises synthesis of PUT-epoxy resin (i.e. DGEBA) (PUT-ER) systems. Then all the glass reinforced composites have been laminated and characterized by chemical, mechanical and electrical properties. The thermal stability of cured systems was also studied by using thermogravimetry analysis. The whole synthetic route is scanned in scheme 1.

Experimental

Materials

Epoxy equivalent weight of Diglycidylether of Bisphenol-A (DGEBA), E-type of glass woven fabric (0.25mm thick) was obtained from Unnati Chemicals, India used for glass fiber reinforcement. All other chemicals used were of analytical grade. Various 2-aminobenzothiazoles were prepared by the methods reported in the literature [20].

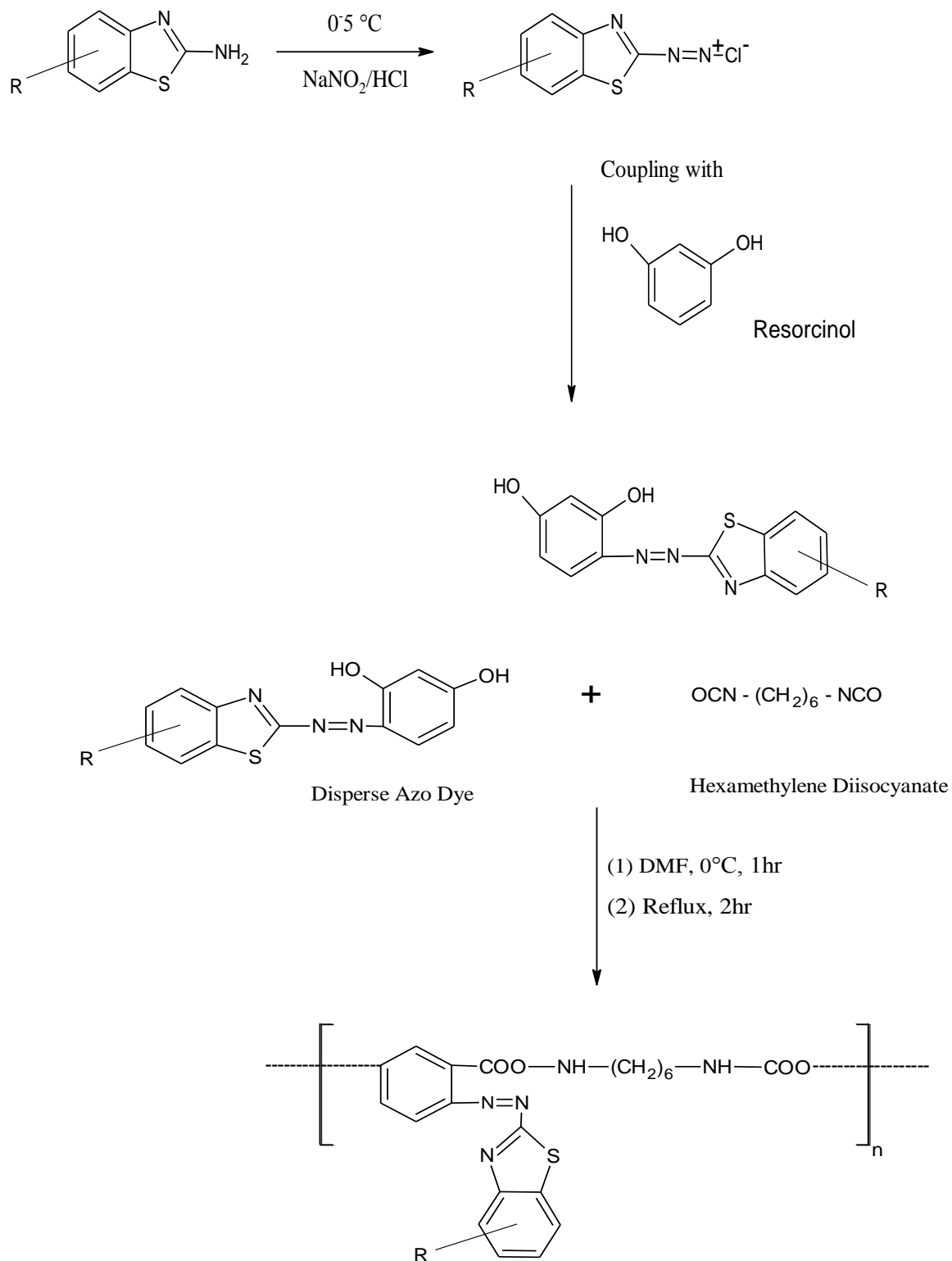
Synthesis of Disperse Dyes containing Polyols

To 5.5 mmol Resorcinol, added 1 ml concentrated hydrochloric acid and 10 ml water to make its salt solution. 5.5 mmol 2-aminobenzothiazoles, 10 ml H₂O and 5.5 mmol NaNO₂, were mixed to form a paste, which was poured into a mixture of crushed ice and 1.5 ml concentrated hydrochloric acid. The reaction was carried out for 0.5 h in an ice bath. The diazonium salt solution was added slowly into the resorcinol solution during stirring and the mixture reacted for 1 h. After neutralizing with ammonia water, the product was filtered and washed with water until neutral [21].

Synthesis of Colored Polyurethanes (PUTs)

All the polyurethanes 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 containing polyol group (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 hour. The resulting solid product was then filtered off and air-dried (95% yields).



Polyurethane
Scheme 1 Synthesis Steps

Where,

R = 6- Cl, 6- OCH₃, 4- CH₃, 6- NO₂, 6-F, H, 6- OC₂H₅, 6-Br

Synthesis and Composite fabrication of PUT-Epoxy Resins Curing Systems

PUT-epoxy resin system has been prepared by mixing each of PUT and epoxy resin (i.e. DGEBA) at stoichiometric ratio. The mixture was stirred well for 15-minutes to form a homogeneous system. Suspension of PUT-epoxy resins (i.e. DGEBA) (PUT-ER) systems were prepared in tetrahydrofuran (THF) and stirred well for ten minutes. The suspension was applied with a brush to 250mm × 250mm phenolic compatible fiber glass cloth and 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 prepregs stacks were cured by heating at $175 \pm 10^\circ\text{C}$ for 4 hours in an air circulated oven. The composite so obtained was cooled to 50°C before the pressure was released.

Measurement and Curing Study

The C, H, N, S contents were estimated by means of Thermofinigen-1101 Flash elemental analyzer (Italy). The sulfur content was determined by Carius method [22]. The IR spectra of all the polymers were scanned in KBr pellets on a Perkin Elemer 257 spectrophotometer. The number average molecular weights (\overline{M}_n) of PUTs were estimated by non-aqueous 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{M}_n) of all polymer samples were calculated following the method reported by one of the author [23]. Thermogravimetric analysis for polymers was carried out on Du Pont thermobalance in air at a heating rate of $10^\circ\text{K min}^{-1}$. The electrical conductivity of each sample was measured on pellets (1cm diameter, 0.45cm thickness) at room temperature using a Million Megohmmeter RM 160 MK IIA BPL, India. The preparations of the pellets of all the PUT samples and other details have been described in an earlier communication [24].

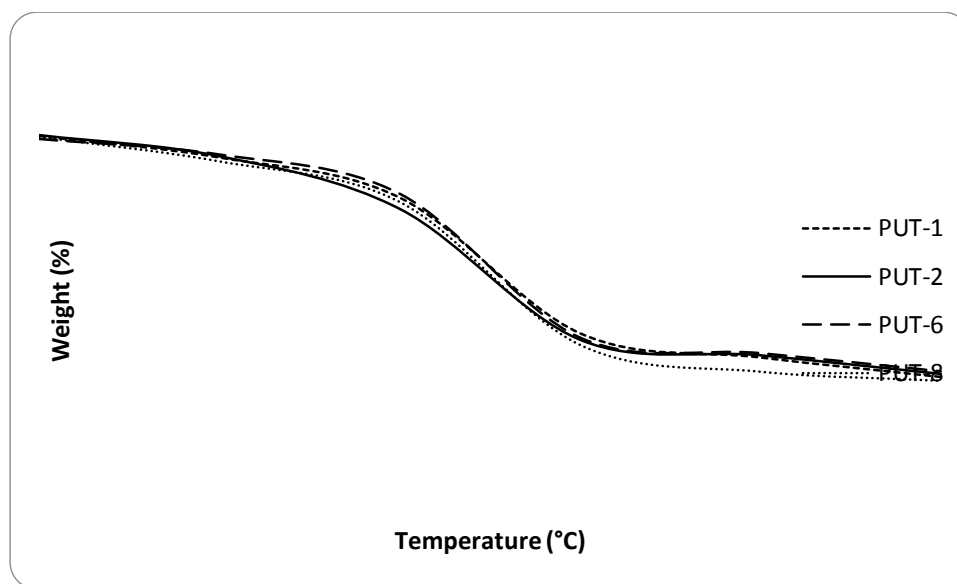


Figure 1 TGA of Polyurethanes (PUT)

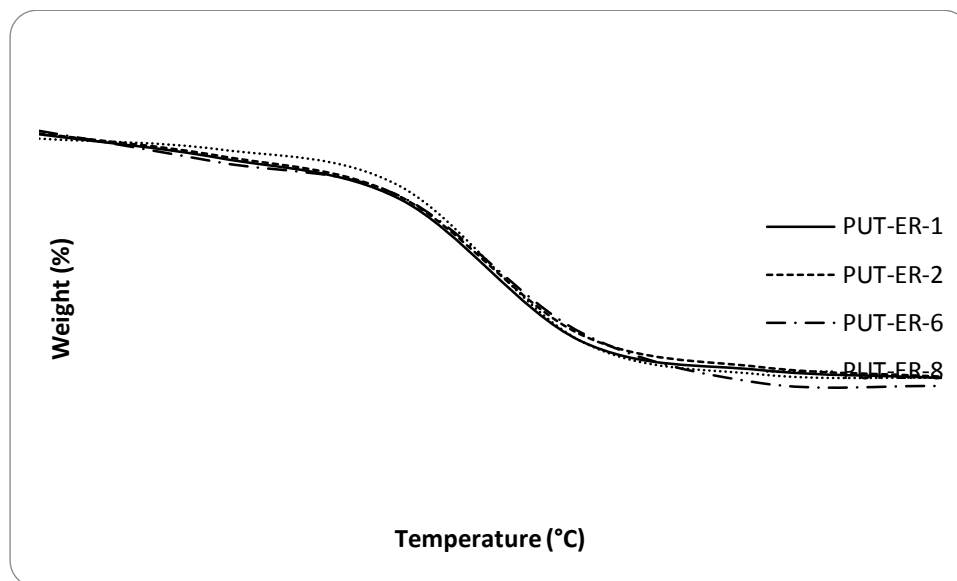


Figure 2 TGA of Unreinforced Cured Polyurethane-Epoxy Resins (PUT-ER) Systems

Curing

A Du Pont 900 DSC was used for the curing study of PUT-epoxy resins (i.e. DGEBA) (PUT-ER) 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 $10^{\circ}\text{C}/\text{min}$ in air. The sample weight for this investigation used 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 ASTM methods. The chemical resistance of the composites towards sodium hydroxide, organic solvents and mineral acids was measured by the method described in the ASTM D543-67. The Flexural strength, Compressive strength, Impact strength, Rockwell hardness and electrical strength were also measured by the method described in ASTM D790, ASTM D695, ASTM D256, ASTM D785 and ASTM D149 respectively.

Results and Discussion

C, H, N, S data (Table 1) of all the PUTs is consistent with the corresponding predicted structure (reaction scheme). IR spectra (Fig. 1) of all the PUTs are identical in almost all aspects. The IR bends at $1700\text{-}1620\text{ cm}^{-1}$ may be due to the urethane 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{M}_n) of all the polymer samples have been measured by end group $-\text{NH}_2$ by non-aqueous conductometric titration. The results of \overline{M}_n values are furnished in Table 1. Thermograms of PUTs and PUT-ERs are shown in Figure 1 and Figure 2. Inspection of the TG thermograms reveals that all the PUTs and PUT-ERs decomposed in two steps. They start their degradation about 200°C , and lose their weight rapidly between 200 to 800°C . The electrical conductivity measured at room temperature of all PUTs samples are shown in Table 2 and are in the range of 6.5×10^{-10} to $7.6 \times 10^{-7}\ \Omega\text{cm}^{-1}$ depending upon the nature of polymer. The examination of the results reveals that the PUTs can be ranked as poor insulators.

The curing study of PUT-epoxy resin (PUT-ER) was carried out by Differential Scanning Calorimetry (DSC). The data obtained from DSC thermograms show that all the cured PUT-epoxy resins (i.e. DGEBA) (PUT-ER) systems give a single exothermic peak in the range 168 to 289°C (Table 3). There was not much variation in the values of activation energy (E_a) for such systems (Table 3). The activation energy (E_a) as a

function of Curing Temperature and order of reaction (n) are furnished in Table 3. The glass reinforced composites based on PUT-epoxy resins (i.e. DGEBA) (PUT-ER) systems were also prepared at $175 \pm 10^\circ\text{C}$ for 4 hours. The density of all the composites was in the range of 1.31 to 1.34 g/cm^3 (Table 4). 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 (1.0 to 1.3%) and a weight loss of about 1.0 to 1.3% was found. Electrical strength of all the composites was found in the range of 12.9 to 17.3 kV/mm. Composite characterizations reveals that composites have good chemical, mechanical and electrical properties.

TABLE 1 Characterization of Polyurethanes (PUTs)

PUT Sample	Mole Formula of Repeating Unit	Mol. Wt. of Repeating Unit	\bar{M}_n	Elemental Analysis			
				%C Fnd (calc)	%H Fnd (calc)	%N Fnd (calc)	%S Fnd (calc)
PUT-1	$\text{C}_{21}\text{H}_{22}\text{ClN}_6\text{O}_2\text{S}$	458	4762	51.89 (55.02)	4.72 (4.80)	18.20 (18.34)	6.86 (6.99)
PUT-2	$\text{C}_{22}\text{H}_{25}\text{N}_6\text{O}_3\text{S}$	454	4348	57.97 (58.15)	5.43 (5.51)	18.43 (18.50)	7.00 (7.05)
PUT-3	$\text{C}_{22}\text{H}_{25}\text{N}_6\text{O}_2\text{S}$	438	5000	60.11 (60.27)	5.64 (5.71)	19.00 (19.18)	7.26 (7.31)
PUT-4	$\text{C}_{21}\text{H}_{22}\text{N}_7\text{O}_4\text{S}$	469	5556	53.63 (53.73)	4.56 (4.69)	20.84 (20.90)	6.77 (6.82)
PUT-5	$\text{C}_{21}\text{H}_{22}\text{FN}_6\text{O}_2\text{S}$	442	6250	56.87 (57.01)	4.86 (4.98)	18.93 (19.00)	7.14 (7.24)
PUT-6	$\text{C}_{21}\text{H}_{23}\text{N}_6\text{O}_2\text{S}$	424	3846	59.35 (59.43)	5.37 (5.42)	19.73 (19.81)	7.46 (7.55)
PUT-7	$\text{C}_{23}\text{H}_{27}\text{N}_6\text{O}_3\text{S}$	468	4000	58.86 (58.97)	5.64 (5.77)	17.82 (17.95)	6.76 (6.84)
PUT-8	$\text{C}_{21}\text{H}_{22}\text{BrN}_6\text{O}_2\text{S}$	502	4762	50.12 (50.20)	4.27 (4.38)	16.66 (16.73)	6.28 (6.37)

TABLE 2 Electrical conductivity of PUTs

PUT Samples	Electrical conductivity (σ) at 303°K ($\Omega\cdot\text{cm}^{-1}$)
PUT-1	4.9×10^{-8}
PUT-2	6.5×10^{-10}
PUT-3	3.8×10^{-9}
PUT-4	7.6×10^{-7}
PUT-5	6.6×10^{-9}
PUT-6	7.1×10^{-7}
PUT-7	6.9×10^{-8}
PUT-8	5.1×10^{-9}

TABLE 3 Curing Characterization of PUT: Epoxy Resins (PUT-ER) Systems

PUT-ER Samples	Kick off Temp. T_i (°C)	Peak Temp. T_p (°C)	Final Temp. T_f (°C)	Activation energy (Ea) KJ/mol	Order of Reaction 'n'
PUT-ER-1	176	201	241	187.9	1.8
PUT-ER-2	169	187	212	198.7	2.1
PUT-ER-3	232	265	289	186.6	2.0
PUT-ER-4	168	194	232	188.6	1.8
PUT-ER-5	202	236	268	194.3	2.0
PUT-ER-6	192	228	269	197.1	1.9
PUT-ER-7	211	242	278	194.2	2.1
PUT-ER-8	171	210	251	189.7	1.8

TABLE 4 Chemical, Mechanical and Electrical Properties of Glass Fiber Reinforced Composites Prepared from PUT: Epoxy Resins (PUT-ER) 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						
PUT-ER-1	1.0	1.3	1.34	253	225	185	134	14.4
PUT-ER-2	1.1	1.0	1.33	237	240	203	125	17.3
PUT-ER-3	1.3	1.2	1.31	242	218	197	145	14.7
PUT-ER-4	1.1	1.3	1.33	260	235	178	121	13.5
PUT-ER-5	1.2	1.1	1.32	234	224	195	116	12.9
PUT-ER-6	1.3	1.2	1.34	264	238	187	118	16.9
PUT-ER-7	1.0	1.1	1.31	258	252	193	141	15.6
PUT-ER-8	1.2	1.3	1.33	243	230	182	139	16.2

Conclusion

The PUT and PUT-ER systems can be prepared easily. All the prepared composites have glossy surface. The glass reinforced composites of PUT-ER systems have been laminated and showed excellent resistance properties against chemicals and good mechanical and electrical properties. The properties of PUT-ER systems are good then individual PUT and epoxy resins. The laminate prepared from 30/70 wt% ratio of PUT-ER systems produced the best results when impregnated at 145°C for 2.5 min and laminated at 180°C for 34 s under pressure of 24 kg/cm². The laminate prepared from 50/50 wt% ratio of PUT-ER systems produced the best results when impregnated at 140°C for 2.5 min and laminated at 220°C for 23 s under pressure of 24 kg/cm².

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