

Poly (urethane-urea)-Epoxy glass fiber reinforced composites

Medha Joshi^{1*}, Dhaval Desai¹ and Smita Jauhari²

¹ V. S. Patel college of Arts and Science, Bilimora, Gujarat, India.

²SVNIT, Surat, Gujarat, India.

E-mail: mbjoshi0316@gmail.com

Abstract : A series of Poly (urethane-urea)s (PUU)s were synthesized using Toluene 2, 4-diisocyanate, various 2-amino benzothiazoles and 3-amino phenol. All the PUUs were characterized by elemental analysis, spectral studies, number average molecular weight (\overline{M}_n) and thermogravimetry. Further reaction of PUUs was carried out with an epoxy resin (i.e. DGEBA). The curing study of prepared resins was monitored by DSC. Based on DSC thermograms 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).

Keywords : Poly (urethane-urea) s, Epoxy, glass reinforced composites, Thermogravimetry analysis (TGA), Number average molecular weight (\overline{M}_n), Differential Scanning Calorimeter (DSC).

Introduction

Epoxy resins are a class of versatile thermosetting polymers, which are widely used in structural composites, adhesives, surface coatings and electronic circuit board laminates [1]. However, they are brittle and vulnerable to the presence of microcracks that are caused by the mismatch of thermal expansion coefficients between epoxy resins and their surrounding environment or bonded parts. Extensive research has thus been conducted to toughen epoxy [2-3]. 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. [4] followed by numerous other studies. Each of polyureas and polyurethanes are well known candidates for industrial polymer applications [5]. Polyurethane is a widely used polymer with flexible segments for elastic property and stiff segments to provide physical crosslinks for mechanical strength. Polyurea is structurally similar to polyurethane, but its stiff segment ($-HNRNH-$) is much more polar resulting in higher mechanical strength. It was found that polyurea formed thick interface particles, and created an effective toughness improvement—94% increase in fracture toughness [6].

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Looking to the excellent properties of both Polyurethane and polyurea was interesting to study the Poly (urethane-urea) for the highest strength of both Polyurethane and urea. Poly (urethane-urea)s are the most important class of copolyureas. They are prepared from macrodiols (polyester diols, polyether diols, etc and diisocyanate in excess) resulting in prepolymers with NCO end groups which react with diamines (chain extenders). The introduction of both the groups into one polymer chain has not yet received much attention. However only few poly (urethane - urea)s are reported from aminoglucose or from mixture of diol, diamines and diisocyanate [7-8].

In this study the authors have synthesized Poly (urethane-urea) s by the polycondensation reaction between the Disperse Dyes containing –OH and –NH₂ groups and Toluene 2, 4-diisocyanate. Then these Poly (urethane-urea)s were mixed with Epoxy (i.e. DGEBA) to prepare glass fiber reinforced composites. Based on DSC thermograms glass reinforced composites have been laminated and characterized by chemical, mechanical and electrical properties.

Experimental Work

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. Toluene 2, 4-diisocyanate was received from Sigma Aldrich. Various 2-aminobenzothiazoles were prepared by the methods reported in the literature [9].

Synthesis of Poly (urethane-urea) (PUU) and PUU/Epoxy (PUU-E) Composite

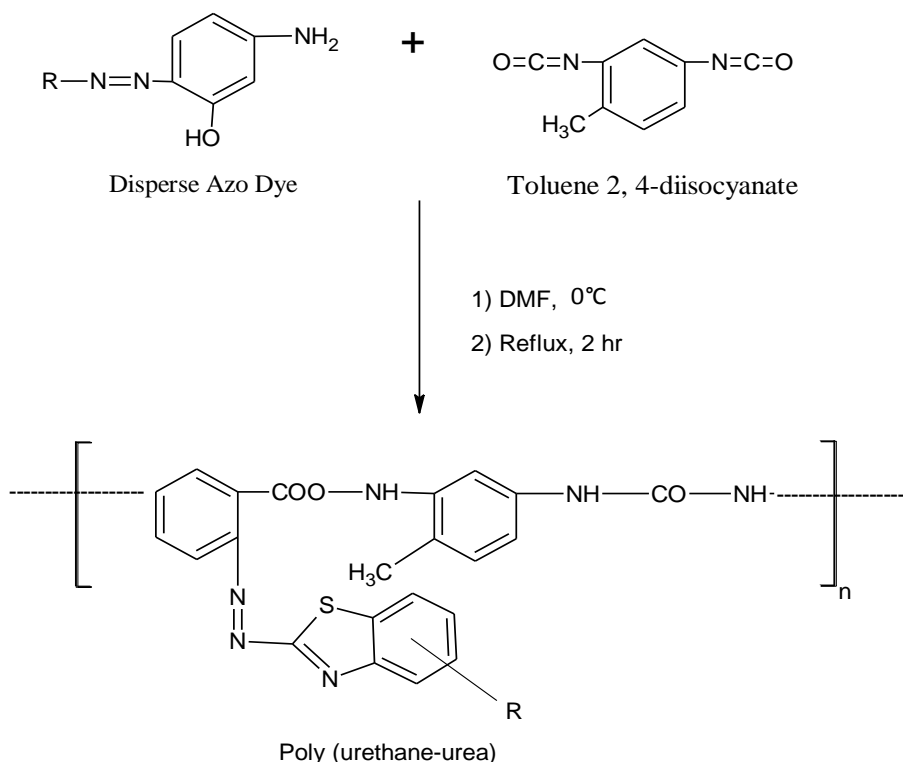
Poly (urethane-urea)s (PUU) were synthesized from Disperse Dyes, synthesized from 3-amino phenol and 2-amino benzothiazole derivatives with Toluene 2, 4-diisocyanate according to our previous procedure [10], was mixed with epoxy (i.e. DGEBA) at stoichiometric ratio. The mixture was stirred well for 15-minutes to form a homogeneous system. Then 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 ± 10°C for 4 hours in an air circulated oven. The composite so obtained was cooled to 50°C before the pressure was released.

Analysis

The number average molecular weights (\overline{M}_n) of PUUs 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 reported method [11]. Fourier transform infrared spectroscopy (FTIR) spectra of PUU samples were recorded between 4000 cm⁻¹ and 400 cm⁻¹ on a Perkin Elmer-983 FTIR spectrometer, FTIR samples were prepared by mixing with KBr. Thermogravimetric analysis for polymers was carried out on Du Pont thermobalance in air at a heating rate of 10°K min⁻¹. A Du Pont 900 DSC was used for the curing study of PUU-epoxy (PUU-E) 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 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. ASTM D 543-67 was used to measure the chemical resistance of the composites towards sodium hydroxide, organic solvents and mineral acids. ASTM D 790, ASTM D 695, ASTM D 256, ASTM D 785 and ASTM D 149 were used respectively to measure Flexural strength, Compressive strength, Impact strength, Rockwell hardness and electrical strength.



Scheme 1 Synthesis Steps

Where,

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

Results and Discussion

Polymer Characterization:

The chemical structures of the poly(urethane-urea)s were verified using FTIR spectroscopy. The amide (–NH) structure in urethane/urea linkages was observed at 3330cm^{-1} in each spectrum. Peaks between 1730cm^{-1} and 1710cm^{-1} correspond to the free carbonyl groups and H-bonded urethane carbonyl groups [12]. The peak around 1645cm^{-1} corresponds to the H-bonded urea carbonyl groups [12]. C–N–H bending in the urethane linkages can be observed around 1545cm^{-1} [13]. Due to the high molecular weight and high soft segment content (between 78% and 84%), a strong sharp peak appears around 1095cm^{-1} that is ascribed to the C–O–C stretching of the ether group [14]. The $2200\text{--}2400\text{cm}^{-1}$ region remained clear, demonstrating that no unreacted isocyanate groups remained [15]. The detailed FTIR spectra are presented in figure 3 for brevity. The other IR spectra features are due to aromatic and aliphatic segments of monomers and appear at their expected positions. The C, H, N, S data (Table 1) of the PUUs are consistent with the corresponding predicted structure (reaction scheme).

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 (\bar{M}_n) of all the polymer samples have been measured by end group –NH₂ by non-aqueous conductometric titration. The results of \bar{M}_n values are furnished in Table 1. The electrical conductivity measured at room temperature of all PUUs samples are shown in Table 2 and are in the range of 9.2×10^{-10} to $8.2 \times 10^{-7} \Omega\text{cm}^{-1}$ depending upon the nature of polymer. The examination of the results reveals that the PUUs can be ranked as poor insulators.

TGA was used to investigate the thermal stability of these poly(urethane-urea)s and to verify the absence of solvent in the samples. There was no indication of any mass loss that could be ascribed to the loss of solvent, so the drying protocol has likely removed all solvent from the polymers. All TGA analysis show similar weight loss, which began between 200°C and 250°C, indicating the onset of polymer decomposition. The H-bonded urea linkages were suggested to provide improved better thermal stability in poly(urethane-urea)s relative to polyurethanes [16,17]. However, thermal degradation following breaking of H-bonds should not cause weight loss in these poly(urethane-urea)s because the H-bond dissociation temperature is much lower (no more than 130°C) [18]. The thermal degradation in TDI-based poly(urethane-urea)s was suggested to start with cleavage of N–H and C–H bonds in the hard segments [19], and the weight loss caused by decomposition of TDI-based hard segments in polyurethanes was observed at about 245°C [20]. The rapid weight loss between 250°C and 500°C was associated with decomposition of the soft segments [21].

The curing study of PUU-epoxy (PUU-E) was carried out by Differential Scanning Calorimetry (DSC). The data obtained from DSC thermograms show that all the cured PUU-E systems give a single exothermic peak in the range 179 to 299°C. 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 fiber reinforced composites based on PUU-E 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 1.30 to 1.35 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 1.1 to 1.3% was found. Electrical strength of all the composites was found in the range of 13.5 to 16.4 kV/mm . All the mechanical strengths were in the range of about 176 to 288 MPa and Rockwell Hardness was in the range 139 to 152. It shows that the composites have very good mechanical properties. Composite characterizations reveal that composites have good chemical, mechanical and electrical properties.

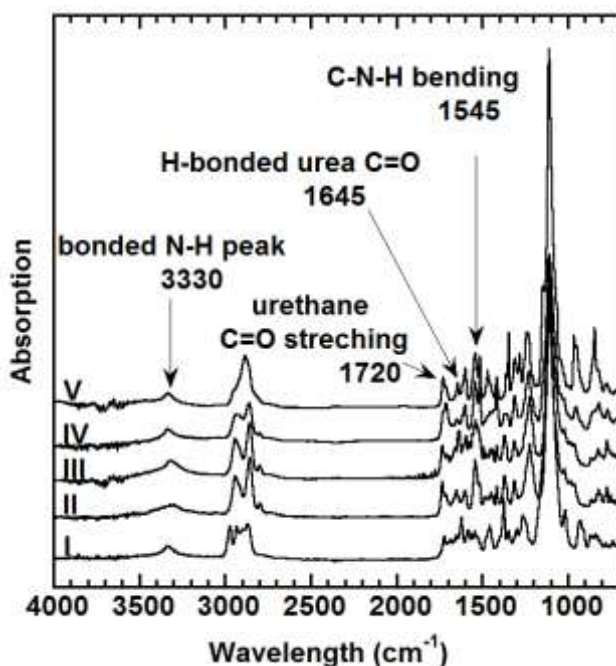


Fig. 1 FT-IR spectra of synthesized poly(urethane-urea)s

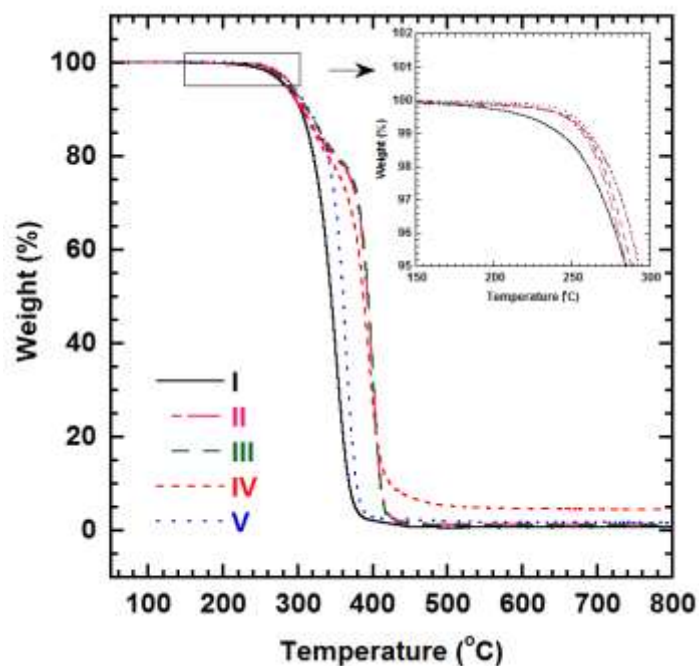


Fig. 2 TGA curves of poly(urethane-urea) s. The heating rate was 5°C/min.

TABLE 1 Characterization of Poly (urethane-urea) s (PUUs)

PUU Sample	\overline{M}_n	Elemental Analysis			
		%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	%S Found (Calcd.)
PUU-1	5000	56.82 (56.90)	3.36 (3.45)	18.01 (18.10)	6.84 (6.90)
PUU-2	4348	59.92 (60.00)	4.03 (4.13)	18.19 (18.26)	6.87 (6.96)
PUU-3	5000	62.09 (62.16)	4.18 (4.28)	18.87 (18.92)	7.16 (7.21)
PUU-4	5556	55.62 (55.70)	3.29 (3.38)	20.60 (20.68)	6.68 (6.75)
PUU-5	6250	59.00 (59.06)	3.49 (3.58)	18.71 (18.79)	7.10 (7.16)
PUU-6	3846	61.50 (61.54)	3.91 (3.96)	19.49 (19.58)	7.40 (7.46)
PUU-7	4762	60.71 (60.76)	4.37 (4.43)	17.65 (17.72)	6.68 (6.75)
PUU-8	4348	51.90 (51.97)	3.09 (3.15)	16.48 (16.54)	6.14 (6.30)

TABLE 2 Electrical conductivity of PUUs

PUU Samples	Electrical conductivity (σ) at 303°K ($\Omega \cdot \text{cm}^{-1}$)
PUU-1	3.2×10^{-8}
PUU-2	6.9×10^{-9}
PUU-3	2.1×10^{-9}
PUU-4	8.2×10^{-7}
PUU-5	6.6×10^{-9}
PUU-6	7.6×10^{-7}
PUU-7	9.2×10^{-10}
PUU-8	5.6×10^{-8}

TABLE 3 Curing Characterizations of PUU- Epoxy (PUU-E) Systems

PUU-E Samples	Kick off Temp. Ti (°C)	Peak Temp. Tp (°C)	Final Temp. Tf (°C)	Activation energy (Ea) KJ/mol	Order of Reaction 'n'
PUU-E-1	192	187	284	188.7	2.0
PUU-E-2	226	265	279	186.6	1.9
PUU-E-3	179	198	245	198.6	2.2
PUU-E-4	211	236	288	194.3	2.0
PUU-E-5	192	228	269	196.1	1.9
PUU-E-6	216	251	282	193.2	2.1
PUU-E-7	214	257	296	187.5	2.2
PUU-E-8	220	264	299	193.7	1.9

TABLE 4 Chemical, Mechanical and Electrical Properties of Glass Fiber Reinforced Composites Prepared from PUU- Epoxy (PUU-E) 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						
PUU-E-1	1.2	1.3	1.35	259	225	199	146	15.7
PUU-E-2	1.3	1.2	1.34	272	236	176	151	13.5
PUU-E-3	1.0	1.1	1.30	254	229	192	139	13.9
PUU-E-4	1.2	1.1	1.34	264	231	188	141	16.2
PUU-E-5	1.2	1.1	1.33	288	258	183	149	15.6
PUU-E-6	1.3	1.3	1.32	246	230	192	152	16.4
PUU-E-7	1.1	1.2	1.35	284	241	196	144	14.8
PUU-E-8	1.0	1.2	1.31	276	253	189	146	16.2

Conclusion

In this research, the composites were prepared by mixing the epoxy and polyurea on the glass fiber cloth. Polyurea was added to the Epoxy to increase the properties and also toughness of the composites. All the prepared composites have glossy surface. The glass reinforced composites of PUU-E systems have been laminated and showed excellent resistance properties against chemicals and good mechanical and electrical

properties. The examination of the electrical conductivity data, results reveals that the PUUs can be ranked as poor insulators.

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