JMEPEG (2012) 21:1346–1351
DOI: 10.1007/s11665-011-9989-x

1059-9495/$19.00

Glass Reinforcement of Various Epoxy Resins-Polyurea Systems

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(Submitted November 22, 2010; in revised form April 15, 2011)

Polyureas (PUs) were prepared by the polycondensation reaction of disperse dyes containing -NH_2 group and toluene 2, 4-diisocyanate. The disperse dyes have been prepared by coupling of various 2-diazobenzothiazoles with 1,3-benzenediamine. All the PUs were characterized by elemental analysis, spectral studies, number average molecular weight $(\overline{\mathrm{Mn}})$, and thermogravimetry. Further reaction of PUs was carried out with an epoxy resin (i.e., DGEBA). The curing study of prepared resins was monitored by differential scanning calorimeter (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). The laminated composites showed excellent resistance properties against chemicals and good mechanical and electrical properties.

Keywords differential scanning calorimeter, glass-reinforced composites, number average molecular weight $(\overline{\mathrm{Mn}})$, polyureas, thermogravimetry analysis

1. Introduction

Polyureas (PUs) may be classified as heterochain macromolecules, which contain urea groups in their chain. Although the chemistry and technology of PUs are of recent origin, the chemistry of ureas dates back over 100 years. Linear PUs are thermoplastic polycondensation products with aliphatic or aromatic structures. PUs 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. PUs containing aromatic structures melt near their decomposition temperatures. They are soluble in some organic solvents and can be used for the preparation of lacquers, varnishes, and coatings. PUs were first prepared on a commercial scale by I.G. Farben, employing the reaction between diisocyanate and diamines. Today, PUs offered many practical applications as foams, elastomers, adhesives, fibers, etc. The area of colored PUs has not received attention academically even though they contain a number of diamine groups (i.e., capable for reaction with diisocyanate). Having urea groups they are compatible with the thermoplast and can be easily form colored articles even when processed at high temperature (Ref 1).

Epoxy resins are versatile resins having wide range of properties such as adhesion to substrate, corrosion resistance and high tensile, flexural and compressive strengths. Because of the versatile properties exhibited by epoxy resin it has found number of applications (Ref 2, 3). 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. Recently, two types of new materials were reported to toughen epoxy without or with little modulus loss. One uses nanoparticles and another is block copolymers, not pure rubber, as effective particles to toughen brittle polymers with little loss in stiffness. The reactive polymer, being composed of stiff and flexible segments, which increases the particle weight fraction and interface strength via chemical reactions between epoxy and the polymer (Ref 4). Hence, high toughness can be achieved. Polyurethane is a widely used polymer with flexible segments for elastic property and stiff segments to provide physical crosslinks for mechanical strength. PU is structurally similar to polyurethane, but its stiff segment (–HNRNH–) is much more polar resulting in higher mechanical strength. Hence, due to versatile properties of epoxy resins it was interesting to study the reaction between PU and epoxy resin [i.e., diglycidylether of bisphenol-A (DGEBA)] systems. It has been found that epoxy terminal groups, which exist in an epoxy molecule, can react with the end group amine of the PU copolymer. Hence, in extension of this work (Ref 5-7) the present article comprises synthesis of PU-epoxy resin (i.e., DGEBA). Based on differential scanning calorimeter (DSC) thermograms glass-reinforced composites have been laminated and characterized by chemical, mechanical, and electrical properties. The whole synthetic route is scanned in Scheme 1.

2. Experimental

2.1 Materials

Epoxy equivalent weight of DGEBA, E-type of glass woven fabric (0.25 mm 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 (Ref 8).

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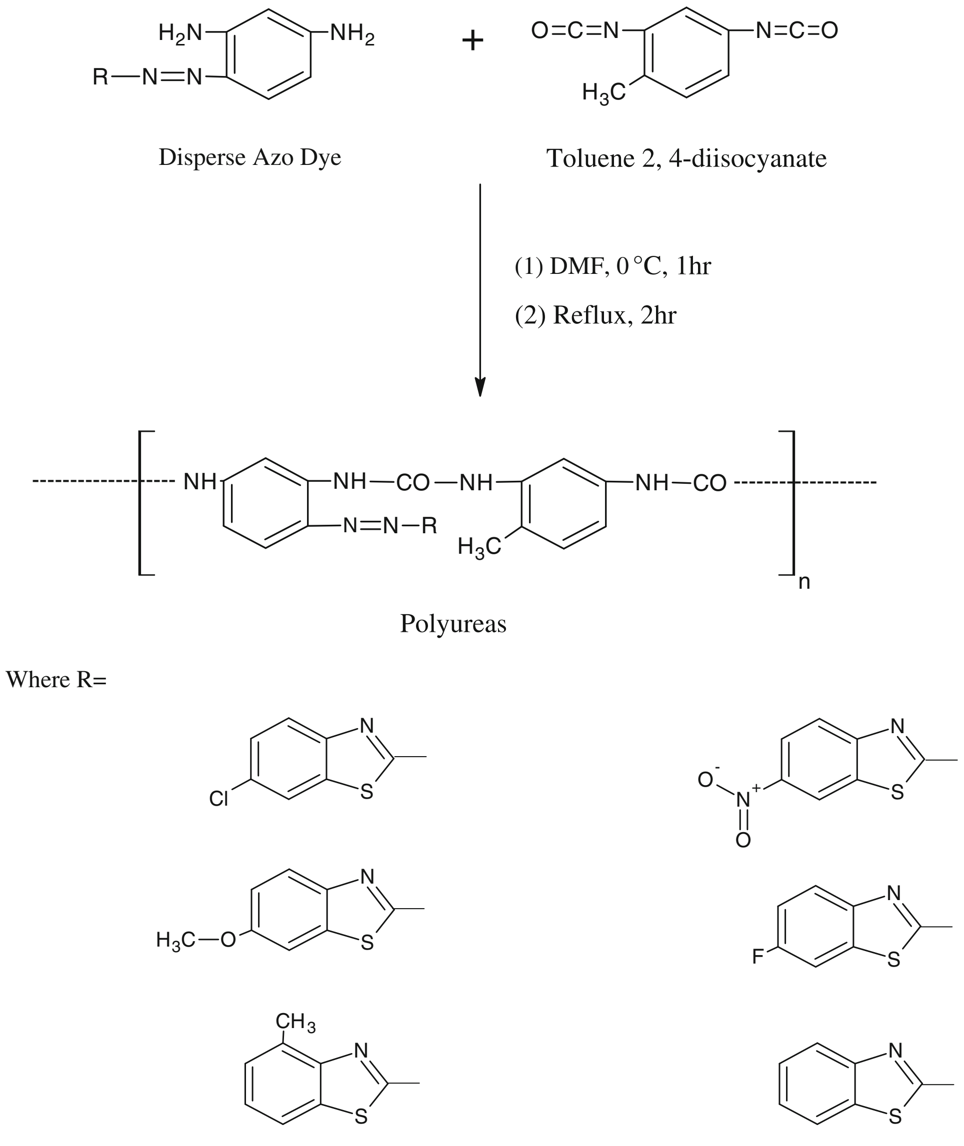

Scheme 1 Synthesis steps

2.2 Synthesis of Azo Disperse Dyes

To 5.5 mmol *m*-phenylene diamine were added 1 mL concentrated hydrochloric acid and 10 mL water to make its salt solution. 5.5 mmol 2-aminobenzothiazoles, 10 mL H_2O and 5.5 mmol $NaNO_2$, 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 solution of *m*-phenylenediamine salt during stirring and the mixture reacted for 1 h. After neutralizing with ammonia water, the product was filtered and washed with water until neutral (Ref 9).

2.3 Synthesis of Colored Polyureas

All the PUs 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 diamines group (0.01 mol) in dry *N*, *N′*-dimethylformamide (50 mL), a solution of toluene 2,4-diisocyanate (0.01 mol) 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).

2.4 Synthesis of PU-Epoxy Resins Curing Systems

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

2.5 Composite Fabrication

Suspension of PU-epoxy resins (i.e., DGEBA) (PUER) systems were prepared in tetrahydrofuran (THF) and stirred well for 10 min. The suspension was applied with a brush to 250 × 250 mm phenolic compatible fiber glass cloth and solvent was allowed to evaporate. The dried 10 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 h in an air circulated oven. The composite so obtained was cooled to 50 °C before the pressure was released.

3. Analysis and Curing Study

The C, H, N, and S contents were estimated by means of Thermofinigen-1101 Flash elemental analyzer (Italy). The sulfur content was determined by Carius method (Ref 10). 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 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 $(\overline{Mn})$ of all polymer samples were calculated following the method reported by one of the authors (Ref 11). Thermogravimetric analysis (TGA) for polymers was carried out on Du Pont thermobalance in air at a heating rate of 10 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

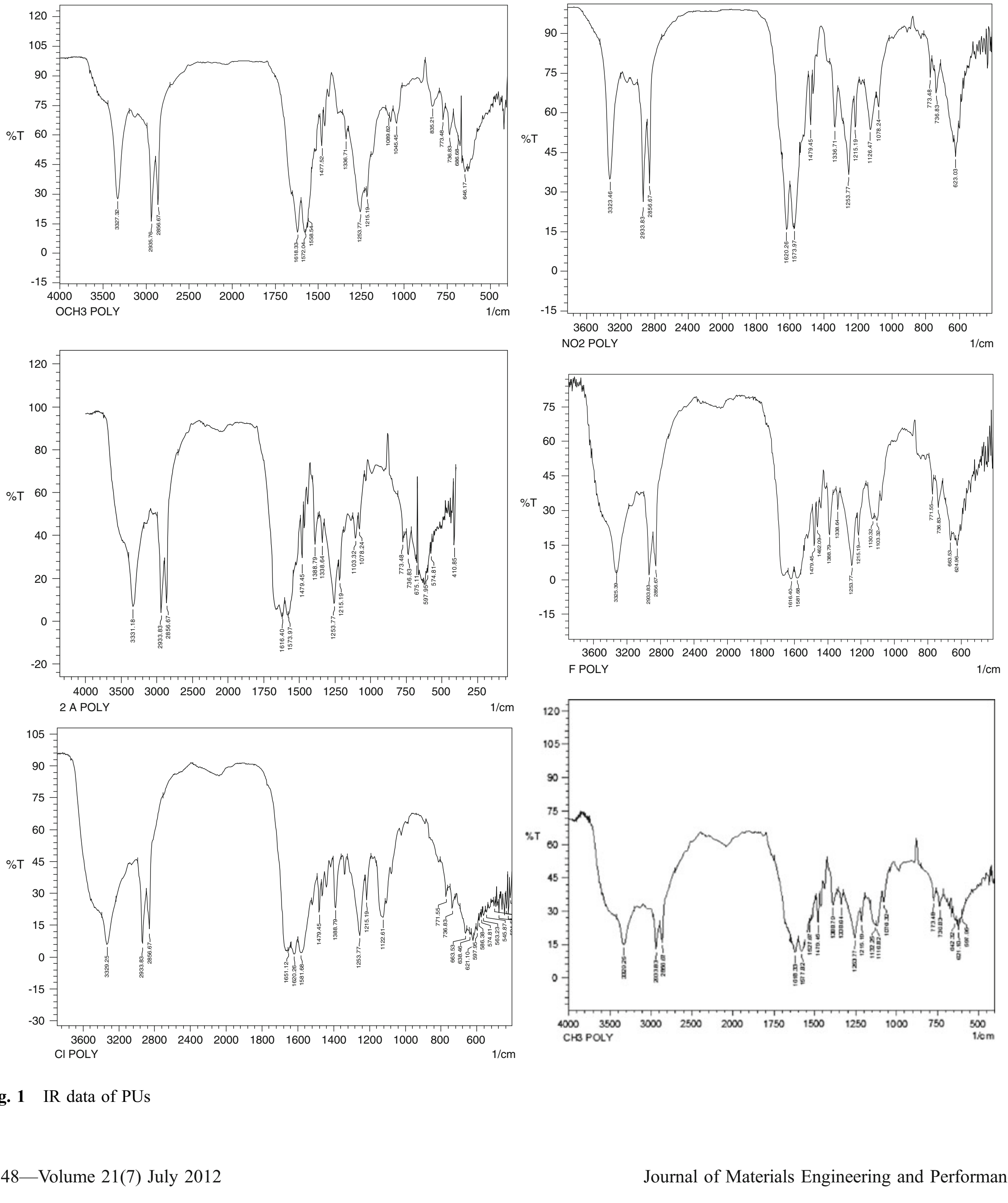

Fig. 1 IR data of PUs

Table 1 Characterization of polyureas (PUs)

PU sample	Molecular formula of repeating unit	Mol. wt. of repeating unit	$\overline{\mathrm{Mn}}$	Elemental analysis Found (Calcd.) %C	 %H	 %N	 %S
PU-1	$C_{22}H_{16}ClN_7O_2S$	478	3824	55.23 (53.28)	3.35 (4.65)	20.50 (20.72)	6.69 (6.77)
PU-2	$C_{23}H_{19}N_7O_3S$	474	4740	58.23 (56.29)	4.01 (5.33)	20.68 (20.90)	6.75 (6.82)
PU-3	$C_{23}H_{19}N_7O_2S$	458	4580	60.26 (58.28)	4.15 (5.52)	21.40 (21.63)	6.99 (7.06)
PU-4	$C_{22}H_{16}N_8O_4S$	488	3416	54.10 (52.07)	3.28 (4.55)	22.95 (23.14)	6.56 (6.61)
PU-5	$C_{22}H_{16}FN_7O_2S$	461	3688	57.27 (55.14)	3.47 (4.81)	21.26 (21.44)	6.94 (7.00)
PU-6	$C_{22}H_{17}N_7O_2S$	443	3974	59.59 (57.40)	3.84 (5.24)	22.12 (22.32)	7.22 (7.29)

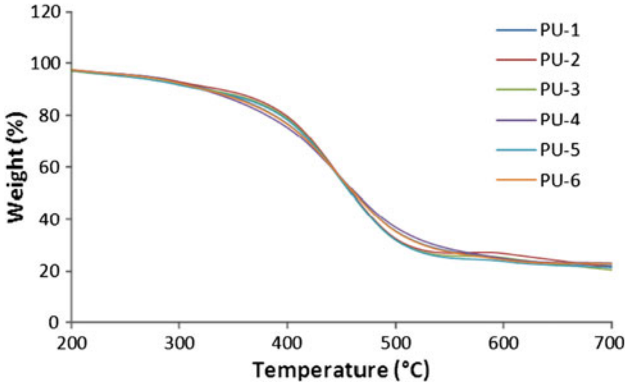

Fig. 2 Thermogravimetric analysis of PUs

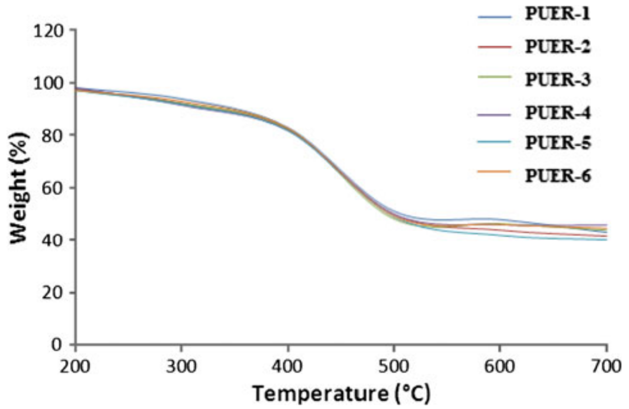

Fig. 3 Thermogravimetric analysis of unreinforced cured PU-epoxy resins (PUER) systems

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 (Ref 12).

3.1 Curing

A Du Pont 900 DSC was used for the curing study of PUER (i.e., DGEBA) curing systems. The instrument was calibrated using standard indium metal with known heat of fusion (ΔH = 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.

Table 2 Electrical conductivity of PUs

PU samples	Electrical conductivity (σ) at 303 K, $\Omega\ m^{-1}$
PU-1	3.2×10^{-10}
PU-2	6.2×10^{-12}
PU-3	2.1×10^{-11}
PU-4	7.6×10^{-9}
PU-5	6.6×10^{-11}
PU-6	7.6×10^{-9}

4. Composite Characterization

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

4.1 Chemical Resistance Test

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

4.2 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.

5. Results and Discussion

The PUs formation is performed by facile reaction of $–NH_2$ group's moiety with –NCO groups. In general, all PUs are found to be colored powders. They do not melt up to 250 °C

Table 3 Curing characterizations of PU-epoxy resins (PUER) systems

PU samples	Kick off temp. Ti, °C	Peak temp. Tp, °C	Final temp. Tf, °C	Activation energy (E_a), kJ/mol	Order of reaction '*n*'
PUER-1	148	175	194	196.6	1.9
PUER-2	156	168	193	194.7	2.0
PUER-3	153	165	199	191.1	2.1
PUER-4	148	176	200	189.6	1.8
PUER-5	153	179	207	195.3	2.0
PUER-6	149	168	190	188.1	1.9

Table 4 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, kg/m^3	Flexural strength, MPa	Compressive strength, MPa	Impact strength, MPa	Rockwell hardness, R	Electrical strength (in air), kV/mm
	Thickness	Weight						
PUER-1	1.17	1.20	1.34	317	318	316	132	18.3
PUER-2	1.13	1.17	1.33	310	312	314	130	18.1
PUER-3	1.13	1.14	1.31	316	314	317	131	18.2
PUER-4	1.17	1.18	1.33	309	306	310	128	17.8
PUER-5	1.18	1.21	1.32	319	319	320	135	18.4
PUER-6	1.19	1.18	1.34	322	322	324	139	18.5

and are insoluble in common organic solvents. C, H, N, and S data (Table 1) of the PUs are consistent with the corresponding predicted structure (reaction scheme).

IR spectra (Fig. 1) 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 bends at 1620-1280 cm^{-1}, 1240-1250 cm^{-1} may be, respectively, 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 and osmometry) have not been studied and hence the number average molecular weight $\left(\overline{\mathrm{Mn}}\right)$ of all the polymer samples have been measured by end group –NH$_2$ by non-aqueous conductometric titration. The results of $\overline{\mathrm{Mn}}$values are furnished in Table 1.

Thermograms of PUs and PUERs are shown in Fig. 2 and 3. 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 and 600 °C.

The electrical conductivity measured at room temperature of all PUs samples are shown in Table 2 and are in the range of 6.2×10^{-12} to 7.6×10^{-9} Ω m^{-1} depending on the nature of polymer. The examination of the results reveals that the PUs can be ranked as poor insulators.

The curing study of PU-epoxy resin (PUER) was carried out by DSC. The data obtained from DSC thermograms show that all the cured PUER (i.e., DGEBA) systems give a single exothermic peak in the range 148-196 °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 PUER (i.e., DGEBA) systems were also prepared at 175 ± 10 °C for 4 h. The density of all the composites was in the range of 1.31-1.34 kg/m^3 (Table 4). Chemical resistance tests revealed that all composites had remarkable resistance properties toward organic solvents and concentrated acids (25% v/v). However, the concentrated alkali (25% w/v) caused changes in their thickness (1.13-1.19%) and a weight loss of about 1.14-1.21% was found. Electrical strength of all the composites was found in the range of 17.8-18.5 kV/mm. All the mechanical strengths were in the range of about 306-324 MPa and Rockwell hardness was in the range of 128-139. It shows that the composites have very good mechanical properties. Composite characterizations reveal that composites have good chemical, mechanical, and electrical properties.

6. Conclusion

The PU and PU-epoxy resin (i.e., DGEBA) systems can be prepared easily. All the prepared composites have glossy surface. The glass fiber-reinforced composites of PUER (i.e., DGEBA) systems have been laminated and showed excellent resistance properties against chemicals and good mechanical and electrical properties. The improved properties of PU-epoxy resin (i.e., DGEBA) systems based composites might be due to the presence of aliphatic ketonic segments and also due to the presence of epoxy resin. The properties of PU-epoxy resin (i.e., DGEBA) systems are better than those of individual PU and epoxy resins.

Acknowledgments

The authors are thankful to Sardar Vallabhbhai National Institute of Technology, Surat for providing the research facility. They are also thankful to Prof. K. R. Desai for providing guidance for the synthesis and Prof. H. S. Patel for providing instrumental facilities and valuable guidance for the application.

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