GLASS FIBER REINFORCED COMPOSITES BASED ON NEWER POLY (UREA-IMIDE)S

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ABSTRACT

Carbon fiber reinforced composites were prepared using PUI-Epoxy resin as a matrix material and carbon fiber as fibrous material. Similarly, glass fiber reinforced composites were prepared by replacing carbon fiber with glass cloth. Both types of composites were characterized for mechanical and electrical properties and chemical resistances. The poly (urea-imide) was prepared by condensation reaction using an equimolar ratio of an amino terminated oligoimide with various aliphatic diisocyanates. The PUIs were characterized by elemental analysis, the number average molecular weight estimation and thermogravimetric analysis. The cure reaction of an epoxy resin with PUI was monitored by differential scanning calorimetric method.

Key words : Hexa methylene bismaleimide (HBM); Poly (urea-imide)s, PUIs; Thermogravimetric analysis (TGA); glass fiber reinforced composite (GFRC); Carbon fiber reinforced composite (CFRC).

INTRODUCTION

Many polymers are particularly suitable as components of composite materials as they adhere readily to the fibers. Thermosetting resins such as epoxides, polyesters, phenolics, silicones and tri-allyl cyanurates are most widely used for the structural applications. One wide class of composite materials in used is the carbon fiber reinforced composites using epoxy resin as a matrix material. Bismaleimide based polymers are prime candidates as matrix resins for advanced composites. To achieve specific combinations of properties, different types of reactants and reaction routs have been used to synthesize tailored maleimide resins. The resins based on the Michael addition reaction using higher molar ratios of bismaleimide to diamine have been well documented. The curing of the resin achieved with bismaleimide double bonds. Thermally stable materials are also obtained, called oligoimide. They have terminal amino' groups that make them suitable for further reaction such as an amidation. The amidation of such amino terminated oligoimide with disocyanates can afford poly (urea-imide). Only few report of PUI based on amino terminated oligoimides are available. Recently, the Indian scientists Patel et al studied amino terminated synthesized by Michael addition reaction of diamines and bismaleimide and their modification with epoxy resin with a view to the above, objective it was though to interesting to extend the PUI based on these amino terminated oligoimides and disocyanates. The present research paper comprises the synthesis and characterization of PUI containing methane groups. The composites are prepared using PUI-epoxy resin system as a matrix material. The research paper has been summarized in scheme I.

EXPERIMENTAL

Materials

4,4' Diamino diphenyl methane an Hexa methylene diamine were obtained for SD fine chemicals, Boisar, India, Hexa methylene bismaleimide (HBM) was prepared by reported methods. A commercial epoxy resin (DGEBA) was obtained from Synpol products Pvt. Ltd., Ahmedabad, India. The Physical properties of the resin were : the epoxy equivalent weight, 190-210; viscosity at 25°C, 4-1 Cp; density at 25°C, 1.16-1.17 g/cc. E-glass woven fabric (polyimide compatible) of 0.25 mm thick (Unnati chemical, Ahmedabad, India) of areal weight...
270 g/m² was used for laminate preparation. Carbon fibers (12K) were obtained from Indian petrochemical corporation Limited, Baroda India.

**Synthesis of oligoimide**

The HBM-DDM oligoimide at 1:2 molar ratio of was prepared by the Michael addition reaction of Hexa methylene bismaleimide (HBM) and 4,4’-diamino diphenyl methane (DDM) by reported method.

**Synthesis of poly (urea-imide)**

A mixture of oligoimide HBM-DDM (0.01 mole), an aliphatic diisocyanates (listed in scheme 1, table 1) (0.01 mole) and potassium hydroxide (catalytic amount) in THF - ethanol (70:30 v/v) mixture (50 mL) was refluxed for 4-5 hours on a water bath at 70°C. The product was then cooled and poured into a large quantity of water-methanol (75:25 v/v) mixture, filtered and washed with THF (10 mL) and then with DMF (10 mL) to remove unreacted reactant. Thus, the poly (urea-imide) was obtained in the from of a dark brown amorphous powder. The details of all PUIs prepared in a similar method are furnished in Table 1.

**Composite fabrication**

The glass and carbon fiber reinforced composites based on PUI-epoxy system were prepared by the reported procedure. A mixture of equimolar proportion of PUI and epoxy resin (40% weight of total glass cloth) in dioxane was stirred well for 2 to 5min. The suspension was then applied with a brush on to a 150 mm x 150 mm polymide compatible fiberglass cloth, and the solvent was allowed to evaporate. Once dried; the ten prepreg were stacked one on top of another, pressed between steel plates coated with a Teflon film, release and compressed in flat platens under about 80 psi pressure. Heating them at 180-185°C for 1h in an air-circulated oven cured the prepregs. The composite so obtained was cooled at 45°C before the pressure was released. Cutting the composites and machining them to final dimension made test specimens.

**Measurements**

The C,H,N,S contents for all the PUIs were estimated by the means of Carlos Erba Elemental Analyzer (Italy).

The number average molecular weight of all PUIs were estimated by non-aqueous conductometric titration methods reported in literature. Non-aqueous 85:15 (v/v) formic acid-acetic mixture was used as the solvent ard standard (0.1M) per chloric acid in acetic was used as a titrant. A digital conductivity meter (Toshniwal, India) was used for the titration.

Cure reaction of epoxy resin with PUI was monitored by Du Pont 900 DSC. The instrument was calibrated using standard material of known heat of fusion. Curing was carried out using a single heating rate of 10° K/Mn. The sample weight for this investigation was in the 4 to 5 mg range an an empty cell was used a reference.

Thermogravimetric analysis (TGA) of all PUIs and PUI-epoxy resin cured products was carried out on Du pont thermo balance in air at a heating rate of 10° K/min.

All the mechanical and electrical properties and chemical resistance were determined according to ASTM methods.

**RESULTS AND DISCUSSION**

All the PUIs presented in Table 1 are brown coloured and insoluble in almost all organic solvents. They do not melt up to 250°C, but above, they soften and turn into either chain extended material with very few crosslinks or char. The elemental analysis of all PAI s is consistent with their predicate structure (Scheme 1). All PUI show positive in the qualitative imide and amide tests. The number average molecular weight of all PUIs estimated by non-aqueous conductometric titration are given in Table 1. Number average molecular weight varied because of the nature of the polymers. Since the PUI are in soluble, so colligative properties like osmometry or viscometer study could not be possible.Hence, only possible method: no aqueous conductometric titration is adopted.

The TGA data of all PUIs is given in Table
Table-1 : Characterization of PUIs based on HBMDMM oligoimide and various diisocyanates

| PUI  | Colour   | Yield | Element analysis | M<sub>n</sub> | %C    | %H    | %N   | Found | Calc'd | Calc'd | Found | Calc'd | Found |
|------|----------|-------|------------------|-------------|-------|-------|------|-------|--------|--------|-------|--------|-------|
| PUI-1 | Dark Brown | 75 | 6885 | 66.28 | 66.20 | 5.58 | 5.60 | 12.25 | 12.11 |
| PUI-2 | Dark Brown | 86 | 6995 | 66.52 | 66.50 | 5.89 | 5.80 | 12.92 | 12.90 |
| PUI-3 | Dark Brown | 82 | 7020 | 67.11 | 67.10 | 7.21 | 7.20 | 13.04 | 13.06 |
| PUI-4 | Dark Brown | 77 | 6995 | 69.49 | 69.50 | 5.83 | 5.85 | 11.57 | 11.50 |
| PUI-5 | Dark Brown | 81 | 7020 | 67.11 | 67.10 | 7.21 | 7.20 | 12.04 | 12.01 |

* Diisocyanates : NDI: Napthalene-1,5 diisocynate, TDI: Toluene-2,4-diisocyanate, HMDI Hexamethylene diisocyanate, DIDPM: 4' diisocynate diphenyl methane, IFDI: Isoforane diisocyanate.

# Number average molecular weights of PUIs were determined by non-aqueous conductometric titration method.

Table-2 : TGA data of PUIs based on HBMDMM oligoimide

| Temp(°C) | 200 | 300 | 400 | 500 | 600 |
|----------|-----|-----|-----|-----|-----|
| PUI-1    | 2   | 14  | 40  | 72  | 89  |
| PUI-2    | 3   | 13  | 41  | 74  | 86  |
| PUI-3    | 4   | 21  | 44  | 71  | 92  |
| PUI-4    | 2   | 14  | 39  | 76  | 90  |
| PUI-5    | 4   | 20  | 38  | 78  | 93  |

Table-3 : Curing Characteristics of PUI-epoxy cured systems (from DSC).

| Temperature (°C) | 133 | 144 | 158 | 33.65 |
|-----------------|-----|-----|-----|-------|
| PUI-1           | 130 | 145 | 162 | 35.12 |
| PUI-2           | 137 | 151 | 168 | 35.64 |
| PUI-3           | 134 | 152 | 169 | 36.37 |
| PUI-4           | 141 | 162 | 177 | 37.28 |
| PUI-5           | 139 | 150 | 166 | 35.95 |

Table-4 : TGA of unreinforced PUI-epoxy cured materials. (PUI based on HBMDMM oligomide)

| Temperature(°C) | 250 | 300 | 400 | 500 | 600 |
|-----------------|-----|-----|-----|-----|-----|
| PUI-1           | 5   | 8   | 39  | 68  | 95  |
| PUI-2           | 3   | 9   | 37  | 66  | 93  |
| PUI-3           | 4   | 11  | 45  | 69  | 97  |
| PUI-4           | 4   | 9   | 40  | 67  | 96  |
Table 5: Chemical resistances, Mechanical properties and Electrical properties of Glass fiber reinforced composites based on PUI-epoxy system (PUI based on HBMDDM oligoimide)

| Reinforcement | Specific gravity | PUI epoxy Content | %Change on exposure* | Flexural | Compressive | Impact | Rockwell hardness | Dielectric strength |
|---------------|-----------------|-------------------|----------------------|----------|-------------|--------|------------------|--------------------|
|               | ASTM D-792 | % NaOH | ASTM D-790 | MPa | ASTM D-695 | MPa | ASTM D-256 | ASTM D-785 | (KV/mm) |
| PUI-1         | 1.5           | 39           | 1.1          | 1.3     | 208         | 216   | 233   | 138     | 14   |
| PUI-2         | 1.6           | 36           | 1.2          | 1.3     | 252         | 200   | 194   | 128     | 14   |
| PUI-3         | 1.6           | 38           | 1.4          | 1.4     | 238         | 230   | 200   | 136     | 12   |
| PUI-4         | 1.6           | 36           | 1.2          | 1.1     | 203         | 182   | 220   | 135     | 12   |
| PUI-5         | 1.6           | 37           | 1.3          | 1.4     | 219         | 186   | 209   | 140     | 13   |

* Unaffected by organic solvents and by (25% w/v) concentrated mineral acid (ASTM D-543 method) ©Reinforcement: E-type Glass cloth, plain weave 10 mm, 10 layers. PUI content: 40±5 weight%, curing temperature: 140±2 °C, curing time: an hour, curing pressure: 80-90 psi, composite size: 150 mm x 150 mm x3 mm.

Table 6: Chemical resistances, Mechanical properties and Electrical properties of Carbon fiber reinforced composites based on PUI-epoxy system (PUI based on HBMDDM oligoimide)

| Reinforcement | Specific gravity | PUI epoxy Content | %Change on exposure* | Flexural | Compressive | Impact | Rockwell hardness | Dielectric strength |
|---------------|-----------------|-------------------|----------------------|----------|-------------|--------|------------------|--------------------|
|               | ASTM D-792 | % NaOH | ASTM D-790 | MPa | ASTM D-695 | MPa | ASTM D-256 | ASTM D-785 | (KV/mm) |
| PUI-1         | 1.3           | 37           | 1.2          | 1.9     | 174         | 167   | 168   | 115     | 12   |
| PUI-2         | 1.2           | 36           | 1.7          | 1.6     | 164         | 160   | 165   | 119     | 14   |
| PUI-3         | 1.5           | 38           | 1.5          | 1.5     | 171         | 174   | 175   | 111     | 14   |
| PUI-4         | 1.1           | 37           | 1.9          | 1.9     | 166         | 183   | 161   | 117     | 13   |
| PUI-5         | 1.3           | 36           | 1.6          | 1.4     | 126         | 166   | 167   | 114     | 12   |

* Unaffected by organic solvents and by (25% w/v) concentrated mineral acid (ASTM D-543 method) ©Reinforcement: Carbon fiber(12K) of 30 tow (of 12” each) 10 layers. PUI-resin content: 40±5 weight%, curing temperature: 140±2 °C, curing time: an hour, curing pressure: 80-90 psi, composite size: 150 mm x 150 mm x3 mm.

2. The PUIs decompose rapidly after 400°C and lose almost 90% of their masses at 700°C.

The cure reaction of PUI-epoxy was studied for the 1:1 molar ratio. The data obtained from DSC scans are furnished in Table 3. From the DSC data, it was seen that all the PUIs-epoxy systems gave a single exothermic peak in the range 150-165°C. The cure onset temperature (Ti), exothermic temperature (Tp) and temperature of completion (Tf) were obtained.

Thermo gravimetric analysis of all the unenforced cross-linked materials reveals that they all degrade in a single step and start their decomposition at around 300°C. Degradation becomes faster between 400°C and 700°C (Table 4).

The glass and carbon reinforced PUI epoxy laminates were dark brown and black sheets respectively. The specific gravity was 1.6-2.0 for glass laminates (table 5) and 1.5-1.8 for carbon laminates (Table 6). Result indicates that there is no appreciable change in the density with the nature of the PUI at the processing temperature. Chemical resistance studied at room
temperature indicating that the PUI glass and carbon fiber laminates were not affected by immersion in organic solvents for 24 hours (alcohols, ketones, DMSO, 1,4-dioxane, THF). No change in weight or thickness was observed. It was also noted that concentrated hydrochloric acid (25% v/v) did not affect the laminates. However, exposure to concentrated alkali (25% w/v NaOH). Resulted in change in thickness and weight (Tables 5 and 6). The high chemical resistance of all laminates indicates that the PUI might contribute to the high level of cross-linking of epoxy resin during laminate fabrication. The mechanical properties of glass and carbon reinforced composites are given in Tables 5 and 6. The results show that the glass composites had somewhat better properties than the carbon ones. This may be due to glass composites being prepared by using glass cloth while carbon composites being prepared by filaments. The value are quite comparable with those from other resin system (phenolic, amino resin). Few poly (urea-imide)s are commercially available and of these only Torlon® has superior properties. Comparison of the mechanical properties of the present laminates of all PUIs with those of Torlon® reveals the they have slightly lower values. The different may be due to the cross-linked network. However, Torlon® has a linear and symmetric polymeric structure.

The electric breakdown potential of all composites is presented in Table and S and 6 for glass and carbon composites respectively. The lower values for the present composites indicates that the composites are insulated.

CONCLUSION

Addition of the epoxy resin to PUIs having some - NH-and-NH-CO- groups increased the toughness of the composites. PUIs have good resistance to organic solvent and mineral acids. The PUIs- epoxy resin system good adhesion to glass and carbon fiber. Void free sheets could be prepared with good mechanical properties.

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