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Glass-reinforced composites based on novel oligoimide–epoxy resin system

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Abstract. A novel matrix resin system, viz. oligoimide–epoxy resin, has been developed to prepare glass-fibre-reinforced composites. Diaminodiphenylmethanebismaleimide–diaminodiphenylmethane (DDMBM-DDM) and *p*-phenylenebismaleimide–diaminodiphenylmethane (PBM–DDM) oligomers having more $-NH_2$ groups were prepared through Michael addition reaction. These oligoimides were used for curing commercial epoxy resin (i.e. diglycidyl ether of bisphenol A) at 120–140°C to fabricate crosslinked oligoimide–epoxy resin glass-fibre-reinforced composites without evolution of byproduct. The fabricated composites (i.e. laminates) were characterized by their chemical resistance and mechanical properties.

Keywords. Epoxy resin; oligoimide; glass-fibre-reinforced composites; mechanical properties of composites.

1. Introduction

Among the thermally stable polymers, polyimides are widely accepted for their outstanding high-temperature properties. However, their high softening temperature and insoluble nature in most organic solvents make them extremely difficult to process, especially into fibre-reinforced composites. To achieve both the temperature performance of polyimide and the processing ease of epoxy resin, we reported (Patel and Shah 1993) recently the oligoimide–epoxy resin curing system. It was observed that such a novel oligoimide–epoxy resin curing system could be processed easily. This paper reports glass-reinforced composites based on such system and the chemical and mechanical testing of glass-reinforced composites.

2. Experimental

2.1 *Materials*

4,4′-Diaminodiphenylmethane and 1,4-phenylenediamine were obtained from SDS Chemicals. *N*,*N*′-4,4′-phenylenebismaleimide and *N*,*N*′-4,4′-diaminodiphenylmethanebismaleimide were prepared by the method reported earlier (Searl and Arnold 1944; US Patent 1949; Crivello 1976). Commercial epoxy resin, viz. diglycidyl ether of bisphenol A (DGEBA) was obtained from Synpol Products Pvt. Ltd, Ahmedabad, India. The specifications of the epoxy resin are as follows: epoxy equivalent weight 190–210; viscosity 4–10 P at 25°C; density at 25°C 1·16–1·17 g/cm^3. E-type fibreglass woven fabric (polyimide compatible) of 0·25 mm thickness (Unnati Chemicals, India) of arral weight 270 g/m^2 was used for laminate preparation.

2.2 *Preparation of oligomers*

N, *N*′-4,4′-diaminodiphenylmethanebismaleimide–4,4′-diaminodiphenylmethane (DDMBM-DDM) and *N*,*N*′-4,4′-phenylenebismaleimide–4,4′-diaminodiphenylmethane (PBM–DDM) oligomers were prepared by the method reported in our earlier communication (Patel and Shah 1993).

2.3 *Composite fabrication*

A suspension mixture of DDMBM–DDM–epoxy resin and PBM–DDM–epoxy resin in tetrahydrofuran was prepared and stirred well for 2 to 5 min. The suspension mixture was applied with a brush on to a 150 mm × 150 mm polyimide-compatible fibreglass cloth and the solvent was allowed to evaporate. Once dried, the 10-plies of prepreg thus prepared were stacked one on top of another, pressed between steel plates coated with a Teflon film release and compressed in a flat platen press under about 70 psi pressure. The prepreg stack was cured by heating in the press to 120–140°C for 12 h. The composite so obtained was cooled to 45°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions. All the chemical, mechanical and electrical tests were conducted according to ASTM or IS methods.

3. Measurements

3.1 *Chemical resistance*

The chemical resistance of the composite was measured according to ASTM D543. The sample size was approximately 20 mm × 20 mm. The data are included in table 1.

3.2 *Mechanical properties*

All the mechanical properties were measured on three individual specimens and the average results have been documented.

3.2a *Flexural strength test*: The measurement of flexural strength of composites were carried out on a Universal Instron testing machine model number A-74·37 at room temperature according to the testing method of ASTM D770. The crosshead speed was 100 mm/min.

3.2b *Compressive strength test*: The compressive strength was measured according to an IS method. The sample size was 12·5 mm × 12·5 mm.

3.2c *Impact strength test*: According to the testing method of ASTM D256, the measurements were made through an Izod-type impact tester at room temperature.

3.2d *Hardness test*: The Rockwell hardness strength was measured according to ASTM D785. The sample size was 25 mm × 25 mm.

Table 1. Mechanical and electrical properties of glass-reinforced composites based on BM–DDM epoxy system.

Resin system	Oligomer epoxy ratio	Percentage change on exposure to 25% (w/v) NaOH Thickness	Weight	Specific gravity	Flexural strength (mPa)	Compressive strength (mPa)	Impact strength (mPa)	Rockwell hardness	Dielectric strength (in air) (kV/mm)
DDMBM:DDM	1:1	1·1	1·2	1·81	266	231	286	123	12·7
(1:1)	1:1·2	1·0	0·9	1·98	116	215	240	122	12·5
DDMBM:DDM	1:1	0·8	0·8	1·59	159	141	152	126	14·7
(1:1·5)	1:1·2	0·9	1·2	1·82	163	179	202	132	13·6
DDMBM:DDM	1:1	1·1	1·0	1·76	158	169	195	136	17·0
(1:2)	1:1·2	1·1	1·3	1·75	175	170	203	136	16·0
PBM:DDM	1:1	0·9	1·1	1·53	292	167	205	121	13·5
(1:1)	1:1·2	0·8	0·9	1·65	207	192	255	125	12·5
PBM:DDM	1:1	1·0	0·8	1·78	125	198	217	117	13·8
(1:1·5)	1:1·2	0·9	1·1	1·87	170	185	131	122	16·7
PBM:DDM	1:1	0·8	1·4	1·74	173	194	175	132	17·2
(1:2)	1:1·2	1·1	1·0	1·93	178	205	168	118	14·4

*Conditions for reinforcement: E glass cloth, plain weave, 10 mm, 10 layers. Resin: fibre ratio: 40:60; Curing temperature 120–140°C; time 12 h; pressure 60–70 psi.
Composite size 150 mm × 150 mm, 3·0–3·2 mm thick.

3.2e *Electrical testing*: Dielectric strength measurements were carried out on a high-voltage tester machine oil test set.

4. Results and discussion

The glass-reinforced oligoimide epoxy composites prepared were in the form of dark brown sheets. The specific gravity of these composites is in the range 1·53–1·98 (table 1). Results indicate that there is no appreciable change in the specific gravity with respect to the nature of the bismaleimide and the processing temperature. Chemical resistance studies indicated that the oligoimide glass fibre composites were not affected by immersion in organic solvents (DMF, ketones, alcohols, 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 composites. However, exposure to concentrated alkali (25% w/v NaOH) resulted in changes in thickness and weight (table 1). The high chemical resistance of all the composites indicates that the bismaleimide moiety might contribute to high level of crosslinking of epoxy resin with oligoimide during composite fabrication.

As described in an earlier communication the unreinforced cure product obtained from oligoimide and epoxy resin are yellow amorphous powders. They did not melt up to 250°C and were insoluble in mineral acids and organic solvents. The film or cast of unreinforced system is too brittle and therefore hardness and other studies are not presented. Since bismaleimides produce a highly crosslinked and brittle polymeric product (Stenzenberger *et al* 1983) they cannot be applied for preparing advanced composites. Several modifications to the bismaleimide system by addition of vinyl monomers, diamines and elastomers have been examined to improve toughness and mechanical properties (Wilson *et al* 1990). Addition of epoxy resin to oligoimide having more epoxy-reactive $-NH_2$ groups may increase the toughness of the final product. Such oligoimide epoxy resins and other polymers have only been patented recently (Saito *et al* 1988) and there is no information regarding the properties of these glass-fibre-reinforced composites. Hence comparison of the mechanical properties of produced glass fibre reinforced composites and those reported about the composites based on bismaleimide resins and epoxy resins individually reveals that the produced laminates have better mechanical properties.

The dielectric strength of all the composites is in the range 12·5–17·2 kV/mm. These values are low. This could result in a charred path, over which subsequent discharge could take place more and more readily. Additionally, minute leakage of current may arise from surface contamination.

5. Conclusions

Combination of versatile polymers, say epoxy resin and bismaleimide resin, could afford the material for advanced glass-fibre-reinforced composites with better toughness and temperature resistance.

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