Effect of Aggressive Environments on Composite Properties

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ABSTRACT: Glass-fiber-reinforced epoxy and unsaturated polyester (UPE) composites were fabricated from diglycidyl ether of bisphenol-A (DGEBA) using 10% diethyl triamine (DETA) as a hardener and unsaturated polyester (UPE) using 1.5% each of methyl ethyl ketone peroxide (MEKP) and cobalt naphthanate as a catalyst and an accelerator, respectively. The fabricated composites were exposed to different aggressive environments, such as heat, water ageing, lubricating oil, fuel, and seawater. The exposed specimens were characterized by physical, chemical, mechanical, and thermal properties. A marginal increase (12%) in the mechanical properties in heat ageing, but a reduction in properties in other exposed systems of the epoxy and polyester glass-fiber-reinforced (GFRP) composites, were observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 795–799, 1999

Key words: cured epoxy; polyester resin; glass fiber; aggressive environment; mechanical properties

INTRODUCTION

The epoxy and unsaturated polyester (UPE) cured resin matrices have gained major acceptance for the fabrication of high-performance composites in the areas of space,[1,2] defense,[3,4] and civilian applications.[5–7] There is limited information about the effect of aggressive environments, such as heat ageing, 95% relative humidity, lubricating oil, fuel, and saltwater spray on composites.[7–10] In this article, the authors have reported physical properties like Shore D hardness, density, and porosity; chemical resistivity; mechanical properties, such as tensile, flexural, and interlaminar shear strength (ILSS); and thermal properties like the T_g of diglycidyl ether of bisphenol-A–diethyl triamine (DGEBA–DETA) and UPE–cobalt naphthanate–MEKP-based glass-reinforced composites before and after subjection to aggressive environments. These studies have been carried out in order to assess their potential use in structural and aerospace applications.

EXPERIMENTAL

Materials

The epoxy resin, DGEBA (Araldite LY 553), and hardener, DETA (HY 951), were obtained from M/s. Cibatul India Limited. The epoxy equivalent weight (EEW) of commercial DGEBA was found to be 190 g/mol with a viscosity of 5000 cPa at 27°C. The polyester resin, HYLAK (HSR 8211), accelerator–cobalt naphthanate (Q-8021), and the catalyst, methyl ethyl ketone peroxide (MEKP) (Q-8013), were obtained from M/s. Bakelite Hylam Limited, India. The above chemicals were used without further purification.

Reinforcement

E-glass fiber cloth, of 0.315-mm thickness, 0°/90° bidirectional, plain weave with specifications IS-5746 type 1, variety 2, was used.

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Fabrication of Composites

The composites were fabricated by a hand lay-up process. Six pieces of resin-impregnated glass cloth were used to get a laminate sheet of 2-mm thickness. The epoxy resin–hardener, DGEBA–DETA of 100 : 10 (weight by weight ratio) was taken. The hardener was dissolved in the epoxy resin at room temperature and stirred well until a homogeneous solution was obtained.

The UPE–cobalt naphthanate–MEKP (100 : 1.5 : 1.5 weight by volume by volume ratio) mixture was taken. The UPE resin was mixed thoroughly with cobalt naphthanate, followed by the addition of MEKP. These mixing processes are highly exothermic in nature.[7]

The ratio between the matrix : fiber was selected on the basis of their wettability. In this study, about 35 : 65 and 38 : 62, matrix : glass fiber ratios were selected for epoxy and polyester systems, respectively. These were the optimized ratios, at which the maximum properties were observed. Epoxy has better wetting characteristics than polyester, as epoxy resin required to wet the same amount of fiber is less than that required by polyester resin. The glass fiber cloth was cut to the size considering the direction along the warp as 0° and that along the weft as 90°. For each layer laid, the resin–hardener mix was applied carefully using the brush as uniformly as possible, and a small roller was used to drive out entrapped air. Six such impregnated plies were stacked together, put between Teflon sheets, placed between two steel plates, and transferred to the platens of the press. A small pressure of 69×10^4 to 103×10^4 N/m^2 was applied until gel time (about 35–45 min). Later, a pressure of around 13.8×10^5 to 16.0×10^5 N/m^2 was applied and allowed at room temperature for 24 h. Spacers of 2 mm thickness were placed between the Teflon sheets to obtain uniform thickness and provide a good surface finish to the laminates.

Characterization of Composites

All measurements were made at 27°C according to ADA standard specifications. About eight replicates were taken for each of the properties, and the average values are reported. The resin content of the laminates were determined by heating weighed samples in a furnace[10] at around 750°C for 3 h. The densities of the laminates were evaluated by ASTM D 792-66 method. Tensile strength, flexural strength, and ILSS were measured according to ASTM 3039, IS-5746, and ADA C-16 test methods, respectively, using a 4301 model hydraullic servo instron universal testing machine. The surface hardness of the laminates was determined by a Shore D hardness testometer. Chemical resistivity in different chemical reagents, namely, acetone, 5% NaOH, 5% HCl, and oxalic acid was measured as per ASTM D 543-67. The dynamic mechanical analysis (DMA) test was done using a DMA-983 Thermal Analyst 2100 of TA instruments USA. Specimens used were $70 \times 10 \times 2$ mm and a span length of 53.8 mm. The DMA run was carried out at a heating rate of 2°C in the temperature range 25–200°C.

Table I Physical Properties of Epoxy and Polyester Glass-Fiber-Reinforced Composite

Properties	Resin Formulations[a] A	B
Fiber : matrix (%)	64 : 36	62 : 38
Density (kg/m^3)	1940	1860
Porosity (%)	4.22	4.89
Surface hardness (Shore D)	96–98	95–97
T_g (°C)	98	149

[a] A represents DGEBA : DETA (80 : 8 wt : wt); B represents UPE : Co. Na : MEKP (90 : 1.3 : 1.3 wt : mL : mL).

RESULTS AND DISCUSSION

Physical Properties

The epoxy and polyester glass-fiber-reinforced composites were characterized for fiber content, density, and porosity. The measured values are given in Table I. Densities of 1940 and 1860 kg/m^3 at 27°C were obtained for epoxy and polyester laminates, respectively. The higher values in density for epoxy composites compared to UPE composites were observed because of higher fiber content and higher specific gravity of the epoxy resin.

From the table, it is evident that porosity values lie in the range of 4.22–4.89% and are in the expected range. The hardness is a measure of resistance to indentation and, hence, will not be greatly influenced by the matrix.[11] The shore D hardness value indicates the percentage of cure.[9] Surface hardness falls in the range of 96–98 and 95–98 for unexposed epoxy and polyester glass fiber laminates, respectively. The values obtained indicate that both the systems were well cured

Table II Mechanical Properties of Epoxy and Polyester Glass-Fiber-Reinforced Composites

Sample Codes[a]	Tensile Strength (N/m^2) $\times 10^7$	Tensile Modulus (N/m^2) $\times 10^8$	Flexural Strength (N/m^2) $\times 10^7$	Flexural Modulus (N/m^2) $\times 10^8$	ILSS (N/m^2) $\times 10^6$
A	26.9	47.9	42.2	24.2	39.2
B	24.5	44.8	31.8	19.4	36.7

[a] A represents DGEBA : DETA (80 : 8 wt : wt); B represents UPE : Co. Na : MEKP (90 : 1.3 : 1.3 wt : mL : mL).

because both the systems have a hardness value greater than 95.[9,11] A slight reduction of about 2–4% in Shore D hardness is observed for exposed systems, except for 70 and 100°C heat ageing. This is attributed to the plasticization effects in other aggressive environments.

Mechanical Properties

The measured tensile strength, flexural strength, ILSS, and modulus at 27°C of epoxy and polyester glass-fiber-reinforced composites are given in Table II. It is observed that the mechanical properties of epoxy glass laminates are superior to those of polyester glass laminates. This can be attributed to the higher fiber content, crosslink density, and good compatibility of the epoxy resin to the glass fiber, which is evident from the ILSS values, which depend mainly upon the nature of the matrix. The values obtained were slightly different for the systems under consideration. A slight improvement or retention of mechanical properties at 70 and 100°C was observed, which is attributed to the increase in crosslink density.[10] A slight decrease in mechanical properties of laminates observed at 120°C is ascribed to the weakening of the chemical bond and interaction between the fiber and matrix at higher temperature. A maximum reduction of 19% in epoxy compared to 3% reduction in polyester laminates was observed because the epoxy had a lower T_g of 98°C compared to the T_g of polyester (149°C).

The reduction in mechanical properties when subjected to 95% relative humidity and seawater spray was due to the plasticization effect and reduced interfacial adhesion between fiber and matrix.[6]

Chemical Resistance

After exposure of the epoxy and polyester laminate specimens to different aggressive environments, such as distilled water, 5% HCl, 5% NaOH, acetone, and 5% oxalic acid for 7 days at room temperature, the exposed specimens were examined for discoloration and loss of gloss. The percentage of weight change is given in Table III.

Aggressive Environment Effect

No appreciable discoloration and loss of gloss was observed for specimens exposed to distilled water, 5% HCl, 5% NaOH, acetone, and oxalic acid. The specimens, after exposing to lubricating oil, 70 : 30 fuel (iso-octane : toluene) and saltwater (seawater) spray were examined for mechanical properties, such as tensile, flexural, and ILSS. The calculated values are presented in Tables IV and V. A slight color change and loss in gloss for specimens exposed to lubricating oil and fuel (70 : 30) are observed. Thus, in specimens treated with different chemical reagents mentioned above, debonding or deformation of bonds takes place, which accounts for the reduction in mechanical

Table III Chemical Resistivity of Cured Epoxy and Polyester Glass-Fiber-Reinforced Composite

Resin System	% Water Absorption (48 h in Boiling H_2O)	Percent Weight Change After Seven Days at 26°C				
		Distilled Water	Acetone	5% NaOH	5% HCl	Oxalic Acid
A	3.82	1.32	0.51	1.03	1.13	1.23
B	3.14	1.28	0.43	0.92	1.16	0.76

Table IV Effect of Aggressive Environments on Mechanical Properties of Cured Epoxy Glass Laminates (Specimens Exposed for 7 Days)

Sample Code	Aggressive Environments	Tensile Strength (N/m^2) $\times 10^7$	Tensile Modulus (N/m^2) $\times 10^8$	Flexural Strength (N/m^2) $\times 10^7$	Flexural Modulus (N/m^2) $\times 10^8$	ILSS (N/m^2) $\times 10^6$
1	70°C	27.7	45.3	42.2	24.1	39.2
2	100°C	27.5	44.9	45.1	25.9	39.2
3	120°C	22.3	38.5	38.1	22.4	39.2
4	95% Relative humidity at 40°C	21.6	35.2	35.3	20.3	39.2
5	Lubricating oil (DERD-2472 at 100°C	22.5	36.7	41.2	22.9	39.2
6	70 : 30 Fuel (iso-octane–toluene) at 70°C	23.5	38.3	40.2	22.4	39.2
7	Saltwater spray (seawater)	22.5	35.8	33.3	19.3	39.2

properties.[7] Exposure of samples to distilled water and seawater also showed reduction in mechanical properties. This is due to the moisture absorbing functional groups, like residual epoxide and/or primary amines in amine network.[12]

A slight improvement or retained mechanical properties were observed at 70 and 100°C heat ageing, but a drastic reduction in properties (>5%) with 120°C heat ageing was observed. This is because of the weakening interaction between matrix and fiber or a reduction in crosslink density of the composite.

Dynamic Mechanical Analysis

The values of T_g obtained from DMA studies are listed in Table VI. The T_g values of DGEBA–DETA after heat ageing are higher than the values before exposing. This is due to the increase in crosslink density.[13,14]

T_g decreases from 98 to 75°C (about 23.4%) in the case of epoxy glass-fiber-reinforced composites and from 149 to 136.8°C (about 8.2%) in the case of polyester glass fiber laminates on exposure to different aggressive environments. A similar trend was observed by McLean et al.[6]

The marginal increase in T_g was observed after heat ageing at 70 and 100°C from 98 to 113°C and from 149 to 151°C for epoxy and polyester GFRC, respectively. This is due to increase in the degree-of-cure and crosslink density. But at 120°C heat ageing, the T_g is reduced. This can be attributed to the degradation of the matrix or weakening of the interaction between matrix and fiber. Table VI shows a maximum reduction of 23.4% in T_g

Table V Effect of Aggressive Environments on Mechanical Properties of Cured Polyester Glass Laminates (Specimens Exposed for 7 Days)

Aggressive Environment Code	Tensile Strength (N/m^2) $\times 10^7$	Tensile Modulus (N/m^2) $\times 10^8$	Flexural Strength (N/m^2) $\times 10^7$	Flexural Modulus (N/m^2) $\times 10^8$	ILSS (N/m^2) $\times 10^6$
1	24.5	44.8	32.4	18.6	36.7
2	24.8	45.2	32.8	18.8	36.7
3	24.0	44.0	31.4	17.4	34.8
4	22.3	40.9	27.7	15.8	33.7
5	22.1	39.5	31.2	17.9	33.9
6	23.1	42.4	29.2	16.8	34.8
7	22.5	40.8	27.6	15.7	33.2

Table VI Effect of Aggressive Environments on the T_g of Epoxy and Polyester Glass Fiber Laminates

Aggressive Environment Code	Epoxy Laminate T_g (°C)	Polyester Laminate T_g (°C)
1	101.2	151.1
2	113.0	150.0
3	110.4	143.0
4	75.0	138.2
5	82.7	138.8
6	83.5	142.3
7	75.0	136.8

values for epoxy laminates and about 8% for polyester laminates. This is because epoxy has a low T_g of (98°C) compared to that of polyester (149°C).

CONCLUSION

The present study reveals that the epoxy laminates used in this study have superior mechanical properties over polyester laminates. There was a reduction in the mechanical properties of the composites after subjecting them to aggressive environments, like 120°C, lubricating oil, 70 : 30 (isooctane : toulene) fuel, 95% relative humidity, and saltwater spray. Water ageing and salt spray greatly deteriorated the mechanical properties. ILSS values were retained by the epoxy laminates, and a slight decrease in properties was observed in polyester laminates when subjected to aggressive environments.

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