FRP Composites Based on Different Types of Glass Fibers and Matrix Resins: A Comparative Study

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SYNOPSIS

Flexural properties, impact energy, heat deflection temperature, and resistance to thermal and hydrothermal degradation of composites based on E-glass and N-glass fibers as the reinforcing agents, and epoxy, unsaturated polyester, phenolic, and epoxy–phenolic resin systems as the matrix materials were studied and compared. As a reinforcing agent E-glass fiber is superior to N-glass fiber, particularly with respect to development of flexural strength and modulus, impact strength, and thermal resistance; N-glass fiber, however, imparts to the composites substantially higher resistance to hydrothermal degradation under boiling conditions in different chemical environments. For use of both E-glass and N-glass fibers as reinforcing agents, the general order of resistance to hydrothermal degradation for the composites based on different matrix resins is epoxy > phenolic > unsaturated polyester resin. Incorporation of a low dose of a rubbery polymer, such as styrene butadiene rubber (0.1–0.2%) and liquid polybutadiene (0.5–0.75%), in unsaturated polyester resin as the matrix resin measurably enhances impact energy of the composite. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The role of a matrix material in a fiber reinforced plastic (FRP) composite is threefold: to transfer stresses between the fibers; to protect the fiber surface from mechanical abrasion and to prevent fiber or fabric dislocation; and to provide a barrier for protection of the reinforcing fiber from the attack of chemical environments.[1]

In achieving high performance and good to excellent balance in the properties for FRP composites, consideration of the properties of each component (fiber and resin/polymer) as well as of the interactions between the components at the interface are of utmost importance. We recently reported[2] comparative features of N-glass and E-glass fibers as reinforcing agents in FRP composites based on isophthalic polyester resin. The present article reports results of similar studies on a comparative basis us-

ing isophthalic polyester resin and some other resins such as general purpose polyester, epoxy, phenolic (cold setting resole), and epoxy–phenolic resins as matrix materials, highlighting mechanical properties developed, thermal response of the relevant composites, and their resistance to hydrothermal degradation under different chemical environments.

EXPERIMENTAL

Materials

E-glass fiber rovings and chopped strand mats (CSM) were supplied by FGP Ltd., India. N-glass fiber rovings and CSM were prepared in our laboratories; the compositions and some physical properties of E-glass and N-glass fibers used are shown in Table I. Epoxy resin (diglycidyl ether of bisphenol A, DGEBA) and its curative, diethylenetriamine (DETA) were obtained from Ciba Geigy of India Ltd. DETA, 15%, was used in the DGEBA. Cold setting, water soluble grade phenolic resole resin (70% solid content) was supplied by Hindustan Ad-

Table I Compositions and Properties of E- and N-Glass Fibers Used in Making Composites

| | Glass Fiber type | |
Constituents	E	N
Chemical composition (wt %)		
SiO_2	54.3	68.41
Al_2O_3	15.2	5.22
CaO	17.2	7.12
MgO	4.7	0.19
Na_2O	0.6	7.84
K_2O	—	3.46
B_2O_3	8.0	6.25
Others	—	1.51
Properties of fibers		
Tensile strength (MPa)	1500	1000
Young's modulus (GPa)	75	65
Density (g/cm^3)	2.54	2.50

hesives and Chemicals, Calcutta. For this resin, p-toluene sulfonic acid (PTSA, 10%) was used as the curative. General purpose unsaturated (o-phthalic) polyester resin (grade HSR 8121) and chemical resistant grade unsaturated (isophthalic) polyester resin (grade HSR 8131), each containing 40% styrene as diluent were obtained from Bakelite Hylam Ltd. The curing agent for each unsaturated polyester resin was a combination of methyl ethyl ketone peroxide (MEKP) (2% of resin taken) and cobalt naphthanate (1.5% of resin taken) (from Bakelite Hylam Ltd.). Epoxy-phenolic compositions were made by mixing the epoxy and phenolic resins as above in 2 : 1 weight proportion using only 20% DETA as curative.

Composite Making

For improved adhesion with matrix resins, both E- and N-glass fibers pretreated with a silane coupling agent (γ-methacryloxypropyltrimethoxysilane, grade A-174 from Union Carbide), following established procedures,[3-5] were used. Resin impregnated rods of diameters 6.5 ± 0.3 mm were prepared using unidirectional rovings (UR) by a hand pultrusion technique employing a Borosil glass tube of appropriate dimension for shaping. Each resin formulation was made by mixing correct doses of appropriate curatives with the resin before impregnation. In each case, curing at room temperature (30°C) was allowed for 72 h followed by postcure in an oven at

70°C for 3 h and then at 100°C for 1 h. Test pieces of 120-mm length were cut from the cured rods. For making composite laminates using N-glass and E-glass CSM, a hand lamination technique was employed taking three mat layers (300 × 300 mm) for each laminate and the manipulation was done to give nearly 35–50% (w/w) glass fiber content in the finally cured laminates. The glass content in the composites was obtained by burning the matrix resin following BS 2782, Part 1-1970, Method 107J. Curing and postcuring for the laminates were done in the same way as for the unidirectional composites. The laminates came in the thickness range of 1.3–2.0 mm and 80 × 13 mm strips were cut out for testing purposes.

Evaluation of Properties

Flexural strength (FS) and flexural modulus (FM) of the composite rods and laminates were determined in an Instron 1185 Universal Testing Machine. Selected rods and laminates were subjected to hydrothermal degradation in distilled water, 10% HCl, 0.5% NaOH, and 10% NaCl solutions under boiling (refluxing conditions) for different time periods. Flexural properties of selected composite rods and laminates were also measured after they were subjected to different specified hydrothermal degradation. An average of five tests in each case were taken for comparison and analysis.

RESULTS AND DISCUSSION

Glass Fiber Content of Composites Made

Results relating to composition of the composites made and their mechanical properties, thermal response, rubber modification, and resistance to hydrothermal degradation are given in Tables II–V and Figures 1 and 2. Table II depicts a range of data for the prepared FRP composites (laminates) highlighting glass fiber content and flexural properties (both initial and after hydrothermal degradation in boiling water for 24 h). For polyester (both general purpose and isophthalic) and epoxy resin based laminates, the maximum glass fiber incorporation by the hand lay-up technique was about 36% while it was about 50% for laminates based on phenolic and epoxy–phenolic resin systems. Much lower viscosity for the water soluble phenolic resin permitted higher incorporation of the glass fiber.

Table II   Flexural Properties of N and E-Glass Fiber Reinforced Plastic (FRP) Composites Subjected to Hydrothermal Degradation Under Boiling Water for 24 h

			Properties of Composites						
			Flexural Strength (MPa)				Flexural Modulus (GPa)		
Matrix Resin Used	Glass Fiber (3 Layers)	Glass Fiber in Composition[a] (wt %)	Initial	After Boiling	Retention (%)	Rate of Strength Loss (% h⁻¹)	Initial	After Boiling	Retention (%)
Polyester									
General purpose	N-N-N	33	180	157	87.22	0.52	9.40	7.80	82.97
	E-E-E	36	205	151	73.65	1.09	10.50	8.00	76.19
Isophthalic	N-N-N	33	215	188	87.44	0.52	10.86	9.75	89.77
	E-E-E	36	229	171	74.67	1.05	11.26	9.50	84.37
Epoxy	N-N-N	33	225	212	94.22	0.24	11.50	10.80	93.91
	E-E-E	36	233	210	90.12	0.41	11.80	10.25	86.86
Phenolic (resole)	N-N-N	50	104	95	91.34	0.36	5.50	5.06	92.00
(Cold setting)	E-E-E	50	114	102	89.47	0.43	6.20	5.40	87.09
Epoxy-phenolic	N-N-N	50	165	150	90.90	0.38	7.50	6.75	90.00
(resole)	E-E-E	50	175	150	85.71	0.59	8.40	7.14	85.00

[a] Glass fibers were all treated with silane coupling agent, A-174 (gamma-methacryloxypropytrimethoxysilane). N, N-glass fiber (CSM 450); E, E-glass fiber (CSM 450).

Resistance to Hydrothermal Degradation in Boiling Water

Comparison of the initial properties data (both FS and FM) clearly indicates that E-glass fiber produces a higher reinforcing effect than N-glass fiber for each resin matrix system used. But loss in the flexural properties on hydrothermal degradation in boiling distilled water is much more severe for E-glass fiber reinforced laminates than for the corresponding N-glass fiber reinforced products, so much so that after 24 h of boiling the flexural properties of laminates based on N-glass fiber become comparable with or even better than those of the E-glass fiber based products.[2] What is more important is that retention of FS and FM as shown in Table II are always higher and the rate of strength loss (% h⁻¹) is uniformly lower for the N-glass CSM laminates.

A comparison between different matrix resins on the basis of the data for the initial FS and FM and those retained after boiling in distilled water for 24 h clearly shows that epoxy resin as the matrix material produces the most resistant composites and the phenolic resin system allows development of relatively poor reinforcing effect (Table II).

Resistance to Hydrothermal Degradation Under Different Chemical Environments

Table III gives a rough comparative idea about the resistance to hydrothermal degradation for the uni-directional composites based on isophthalic polyester, epoxy, and phenolic resins as matrix materials and E-glass and N-glass rovings as reinforcing agents in different aqueous chemical environments (10% HCl, 0.5% NaOH, and 10% NaCl solutions) under boiling. Comparable conditions of pultrusion allowed different degrees of glass fiber incorporation, apparently much as a consequence of differences in the initial viscosity and wetting characteristics of the resin formulations and their initial rate of cure. The differences in initial strength properties of the composites produced also arise partly as a consequence of these differences and partly as a consequence of differences in voids created due to release of volatiles, particularly during postcuring at 100°C. The relative order of resistance of the related composites toward hydrothermal degradation under different chemical environments can be better appreciated by a comparison of the initial rate of fall in strength for the respective composites in the said degradative environments.

Tables II and III clearly show that with respect to resistance to hydrothermal degradation, N-glass fiber based composites are far superior to the corresponding E-glass fiber based composites. For a comparable dose level of glass fiber (Table II), the general order of resistance of the composites based on different matrix resins is epoxy > phenolic > isophthalic polyester. N-glass fiber based composites from each of the three matrix resin materials

Table III Fall or Retention of Flexural Strength (FS) of Unidirectional N- and E-Glass Fiber Reinforced Composites on Hydrothermal Degradation Under Boiling in Different Chemical Environments

Chemical Environment	Glass Fiber in Composite[a]	Isophthalic Polyester Resin (Glass Content 70 ± 2% by wt)			Epoxy Resin (Glass Content 62 ± 2% by wt)			Phenolic (Resole) Resin (Glass Content 50 ± 2% by wt)		
		Initial FS (MPa)	Initial Rate of Fall in FS (% h⁻¹)	Retention of FS after 96 h (%)	Initial FS (MPa)	Initial Rate of Fall in FS (% h⁻¹)	Retention of FS after 96 h (%)	Initial FS (MPa)	Initial Rate of Fall in FS (% h⁻¹)	Retention of FS after 96 h (%)
10% HCl solution	N	972	0.25	91	702	0.18	94	266	0.20	92
	E	1036	2.08	38	703	1.70	40	316	1.84	42
0.5% NaOH solution	N	972	0.33	81	702	0.28	85	266	0.29	83
	E	1036	2.71	30	703	1.36	42	316	1.65	33
10% NaCl solution	N	972	0.07	90	702	0.07	95	266	0.07	93
	E	1036	0.68	43	703	1.56	44	316	1.70	45

a N, N-glass fiber rovings; E, E-glass fiber rovings. Used different synthetic resin as the matrix materials.

exhibit very high and comparable resistance to acid and salt attack (90% retention of strength on boiling for 96 h); but their alkali resistance is not as high, showing 80–85% retention of strength after boiling for 96 h (Table III). However, relevant composites based on E-glass fiber show rather poor resistance to chemicals in general (30–45% retention of strength on boiling for 96 h, Table III). The differences in resistance to hydrothermal attack in different chemical environments between composites based on E- and N-glass fibers are understood[2] to have their origin in differences in the chemical composition of the two fibers, particularly the contents of leachable metal oxides (Table I). Thermal treatment in aqueous chemicals leads to different degrees of undesirable effects such as matrix polymer degradation, fiber–matrix debonding consequent to chemical attack on the fiber surface, etc.[6,7] Strength loss of the glass fiber reinforced composites in boiling chemical environments is caused by an ion exchange reaction involving replacement of cations such as Na^+, K^+, Mg^{2+}, and Al^{3+} near the surface of the glass fiber strands by protons. In view of smaller size of the protons replacing the above mentioned cations, stresses are induced in the surface of the glass that may finally become big enough to promote cracking.[8] Reinforcing fibers from E-glass having a high level of CaO, MgO, and Al_2O_3 content (Table I) are very susceptible to chemical corrosion on exposure to aqueous environments, particularly in acidic condition,[8–10] readily permitting leaching of Ca^{2+}, Mg^{2+}, and Al^{3+} ions from the glass surface.

N-glass fibers have about 20–25% lower content of CaO, MgO, and Al_2O_3 taken together and about 10–11% higher content of alkali metal oxides compared to E-glass. The overall balanced effect is that composites reinforced with N-glass fibers suffer much less corrosion on the fiber surface and hence much lower strength loss in aqueous environments in comparison with E-glass fiber reinforced composites. This also finds support from scanning electron micrograph (SEM) studies.

The SEMs of flexural fractured E-glass and N-glass fiber reinforced polyester composites prior to subjecting them to hydrothermal degradation are shown in Figure 3(A,B) and those of relevant composites subjected to hydrothermal degradation for 24 h in boiling water and for 96 h in dilute alkali solution are shown in Figures 4(A,B) and 5(A,B).

Figure 3(A,B) (micrographs of initial composites) shows almost comparable features of the fractured surfaces showing glass filament bonded together by matrix resin in each case. In Figure 4(A,B), the glass filaments of the E-glass system [micrograph 4(B)]

Table IV   Comparison of Izod Impact Energies of Some Unreinforced Matrix Resins and Fiber Reinforced Composites

Fiber Layers (3 Layers)	Impact Energy (N mm/mm^2)				
	Matrix Resin Used				
	General Purpose Polyester	Isophthalic Polyester	Epoxy	Phenolic (Resole)	Epoxy-Phenolic (Resole)
Unreinforced resin	7.51	8.34	23.72	7.10	14.55
N-N-N	34.39	41.61	62.62	32.07	38.67
E-E-E	38.90	46.94	74.50	35.69	43.17

N, N-glass fiber (CSM 450); E, E-glass fiber (CSM 450). Total fiber content in composites 33–50% by weight (cf. Table II).

suffered apparently higher removal of the matrix resin from the surface due to the action of boiling water; and this chemical action is more severe for dilute alkali attack under boiling conditions as shown in Figure 5(A,B). Here also the removal of the bonding resin and fiber pull-out are more severe for E-glass composites [micrograph 4(B)] than for N-glass composites [micrograph 4(A)]. The initial strength/modulus for the phenolic resin based composites are of a much lower order when viewed against those of the epoxy resin or polyester resin based composites (Tables II, III). This arises partly as a consequence of relatively poor wetting between the hydrophilic phenolic resin and the hydrophobic glass fibers used as the reinforcing agents, and partly as a consequence of generation of a higher degree of voids or porosity due to release of a relatively high proportion of volatile water during curing and post-

cure heating of the composites based on the phenolic resin.

Impact Energy of Composites

Comparative data on the impact energies of the different cured resins and of the corresponding N-glass

Table V   Comparison of Heat Deflection Temperature of Some Unreinforced Matrix Resins and Fiber Reinforced Composites

Reinforcing Fibers Used (6 Layers)	Heat Deflection Temperature (°C)		
	Matrix Resin Used		
	Isophthalic Polyester	Epoxy	Phenolic (Resole)
Unreinforced resin Composites	79	94	130
N	170 (33)	187 (33)	208 (50)
E	194 (36)	200 (36)	210 (50)

N, N-glass fiber (CSM 450); E, E-glass fiber (CSM 450). Data in parentheses indicate weight percentage of reinforcing fiber in composites.
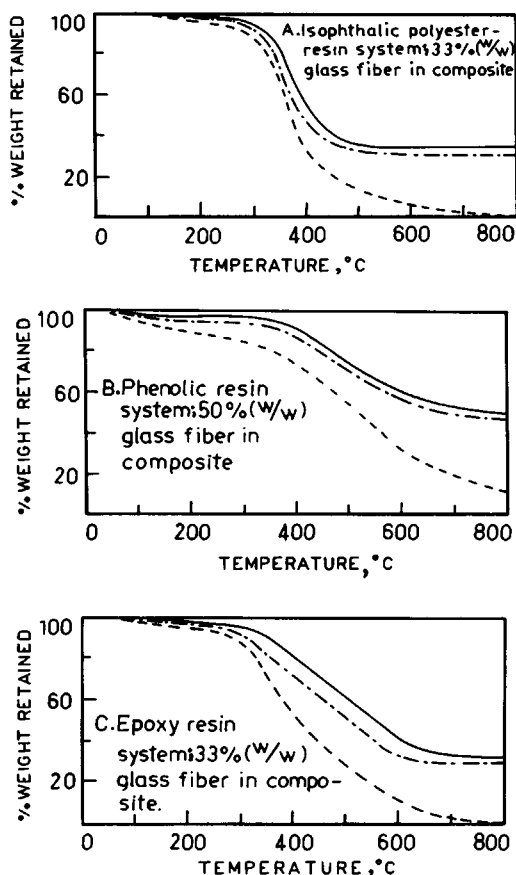
Figure 1   Variation of impact energies of composites based on isophthalic polyester resin with different percentages of (A) liquid polybutadiene rubber and (B) SBR.

Figure 2 TGA thermograms in air at a heating rate of 10°C/min for: (A) cured isophthalic polyester resin and relevant composites, (B) cured phenolic resin and relevant composites, and (C) cured epoxy resin and relevant composites. In each case the identity of the curves are: (---) cured resin, (—) E-glass fiber reinforced composite, and (-·-·-) N-glass fiber reinforced composite.

and E-glass fiber reinforced composites (three ply CSM laminates) as given in Table IV indicate that among the resin systems used, the observed impact energies are in the order epoxy > epoxy-phenolic ≫ isophthalic polyester > general purpose polyester > phenolic resin. In each case, laminates based on CSM from E-glass fiber generally exhibit slightly higher impact energies than those based on N-glass fiber.

Rubber Modification

Attempts were made to improve the impact properties of glass fiber (CSM) reinforced laminates using different small percentages of styrene butadiene rubber (SBR) or liquid polybutadiene (of Brookfield viscosity, 65 Pas at 34°C), each dissolved in styrene

with isophthalic polyester as the matrix resin. Relevant results are shown in Figure 1. The elastomeric polymer content was varied between 0 and 0.4% for SBR and 0 and 2% for liquid polybutadiene. The impact energy is measurably enhanced with low incorporation of the elastomeric polymers and the impact energy enhancement is maximum for incorporation of about only 0.15% SBR and about 0.75% liquid polybutadiene. The impact energy enhancement is of a higher order for use of E-glass fiber CSM than of N-glass fiber CSM as the reinforcing agent. Thus, a very minimal rubber modification of the resin matrix proves to be useful in improving the impact properties of the relevant composites. Incorporation of more than the low optimum dose of the elastomeric polymers as mentioned above leads to progressive fall of impact energy values apparently as a consequence of growing phase heterogeneity developed on curing with MEKP–Co^{2+} redox catalyst.

Uniform dispersion of the rubber in the resin matrix appears to be a serious problem. Poorer disper-
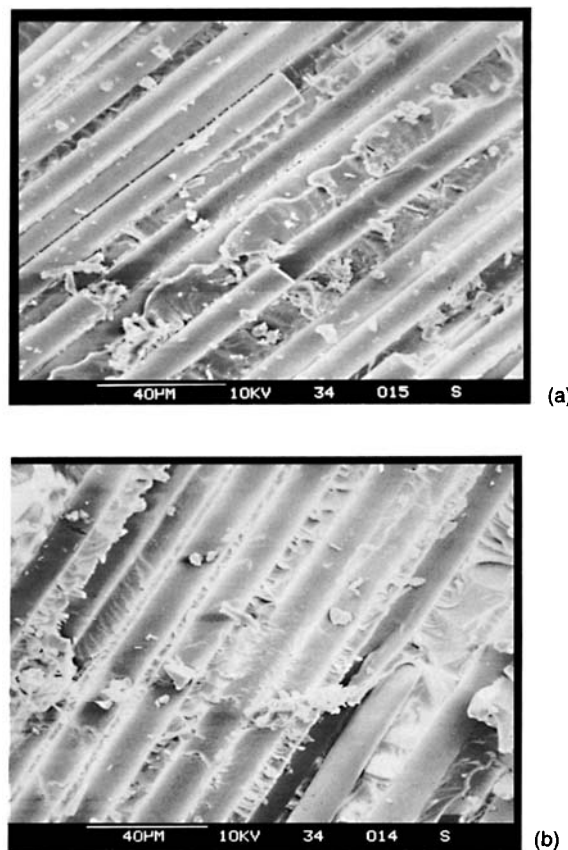
Figure 3 Scanning electron micrographs of (A) N-glass (CSM) and (B) E-glass (CSM) reinforced isophthalic polyester resin based composite laminates, undegraded.
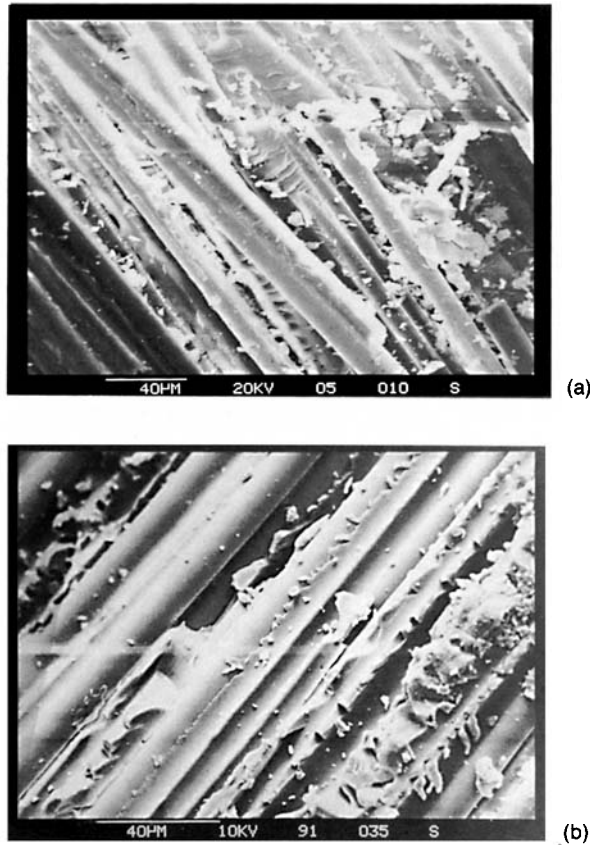
Figure 4   Scanning electron micrographs of (A) N-glass (CSM) and (B) E-glass (CSM) reinforced isophthalic polyester resin based composite laminates, each degraded for 24 h in boiling water.

sion of the elastomeric phase apparently leads to greater phase heterogeneity, particularly after accomplishing curing and hence to poorer impact energy for the corresponding composites. In this context, use of the low viscosity polymer, that is, the liquid polybutadiene, was somewhat more convenient and its incorporation to higher percentages was a lesser problem. The maximum attainable impact energy is marginally higher for incorporation of liquid polybutadiene compared to the incorporation of SBR.

During curing of the unsaturated polyester resin system through polymerization of the styrene monomer used under the influence of the redox (MEKP–Co^{2+}) catalyst, significant incorporation of the rubbery polymer (SBR or polybutadiene used) in the resin network structure by way of graft copolymerization is likely,[11,12] however small that may be under the employed condition. For low incorporation of rubbery polymer, phase heterogeneity remains somewhat restricted partly as a consequence

of grafting of the rubbery polymer with the resin network formed, and partly due to the fact that the concentration of the rubbery polymer is insufficient to give rise to large domain sizes for the resin immiscible rubbery polymer. However, beyond a low optimum concentration for the rubbery polymer, this restriction to gross phase separation no longer holds and as a consequence a dropping trend in impact energy follows.

Heat Deflection Temperature (HDT)

HDT of three selected matrix resins used and those of the corresponding E-glass and N-glass CSM (6 ply) laminates are given in Table 5 which clearly shows that for each matrix resin system, glass fiber reinforcement causes much improvement in the heat deflection temperature.[13,14] Between E-glass and N-glass fibers, the former, showing a better reinforcing effect, produces superior heat resistant composites as well (Table V).
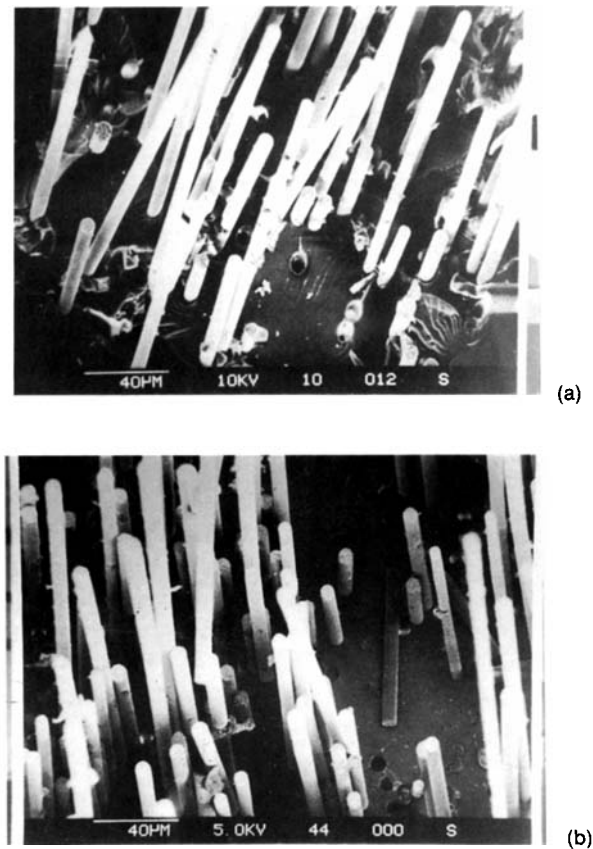
Figure 5   Scanning electron micrographs of unidirectional (A) N-glass and (B) E-glass fiber reinforced isophthalic polyester resin based composites, each degraded for 96 h in boiling 0.5% NaOH solution.

Thermogravimetric analysis (TGA)

The TGA data for the three selected cured resins (epoxy, phenolic, and isophthalic polyester) and of the respective E-glass and N-glass fiber reinforced laminates are shown in Figure 2. Up to about 300°C, the weight loss for epoxy and isophthalic polyester resin is less than and close to 10%, respectively; it is about 18–20% for the phenolic resin. Even though the initial weight loss up to 300°C takes place at a higher rate for the phenolic resin,[15,16] the rate of weight loss in the temperature zone that immediately follows (300–360°C) is substantially lower for the phenolic resin as compared to epoxy and isophthalic polyester resins. The temperature zone over which decomposition at the highest rate takes place is 400–600°C for phenolic resin,[17] 300–500°C for epoxy resin, and 320–400°C for isophthalic polyester resin. Residue left at or beyond 700°C is within 1–2% for epoxy and isophthalic polyester resin and about 15% for the phenolic resin. For each resin system, glass fiber reinforcement results in notable improvement in thermal stability. The weight loss at a given temperature and the maximum rate of weight loss for the glass fiber reinforced composites are lower than those of the corresponding matrix resins. The residue left at or above 700°C nearly corresponds to the weight fraction of the glass fiber in the composites. In each resin matrix system, the weight loss observed on heating at different temperatures is usually lower for E-glass reinforced composites than for the corresponding N-glass reinforced products. It is thus clearly indicated that resistance to thermal decomposition for the composites based on E-glass fibers is measurably higher than that for composites based on N-glass fibers.

CONCLUSIONS

Between E-glass and N-glass fibers used as reinforcing agents in making FRP composites, the former is superior with respect to development of mechanical strength (FS and FM) and resistance to thermal degradation of the initial composites; the latter is superior in imparting to the composites substantially higher resistance to hydrothermal attack under boiling conditions in different chemical environments. For a given reinforcing fiber used in a closely comparable dose in composite making, the mechanical properties order of the matrix resins developed is epoxy > unsaturated polyester > phenolic resin.

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