

Comparative evaluation of N-glass and E-glass fibres with special reference to their use in FRP composites

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The abilities of E-glass and N-glass fibres and of composites based on them to withstand degradative effects in boiling water or in boiling aqueous solutions of HCl (10%), NaOH (0.5%) and NaCl (10%) have been evaluated on a comparative basis by following the loss or retention of strength properties (tensile/flexural) with the time of the respective degradative exposure. The degradative effects under different chemical environments for the composites were also analysed with the help of SEM micrographs of the composites before and after the specific degradative treatments. Analysis of strength properties and retention of strength and of the micrographs clearly indicates that N glass is highly superior to E glass, and the former imparts a much higher order of stability to composites in different chemical environments despite substantial initial advantages in the strength properties for E-glass fibre and composites based on this fibre.

1. Introduction

Glass fibres from E and S glass are used in the fibre-reinforced plastics (FRP) industries. Fibres from another glass type known as C glass are also used in the form of a surface mat to make composites, particularly in chemical plants and equipment where greater corrosion resistance to acid is required. Keeping FRP applications and an overall production economy with respect to glass fibre manufacture in view, another type of glass known as N glass has recently been developed at the Central Glass and Ceramic Research Institute (CGCRI), Council of Scientific and Industrial Research, Calcutta. Comparative compositional characteristics of E, S, C and N glasses are given in Table I. The high silica content and comparatively lower total percentage of oxides of alkali metals and alkaline earth metals for N glass is expected to make this glass more resistant under different chemical environments, particularly in comparison with C and E glasses, and the relatively low alumina content in N glass (compared to E and S glasses) makes it more cost-effective and energy-efficient as far as glass-fibre production is concerned. On cost consideration the fibres based on different types of glass listed in Table I are in the order S glass \gg E glass $>$ C and N glasses [1, 2].

Some preliminary reports [2, 3] have clearly indicated that N-glass fibres are more resistant to acid and alkali compared to E-glass fibres, and composites based on N-glass fibres possess superior wet strength.

Further studies in comparative evaluation of the

stabilities of FRP composites based on N-glass and E-glass fibres as reinforcing agents both as a chopped strand mat (CSM) and as unidirectional rovings (UR) using isophthalic polyester resin as the matrix have been made in our laboratories, and related results are reported in the present paper.

2. Experimental procedure

2.1. Preparation of samples

E-glass fibre rovings and CSM were supplied by FGP Ltd, India. N-glass fibre rovings and CSM were prepared at CGCRI, Calcutta. The isophthalic polyester

TABLE I Glass composition for the production of reinforcement fibres

Constituent	Glass fibre type			
	E	S	C	N
SiO ₂	54.1	65.0	64.6	68.41
Al ₂ O ₃	15.2	25.0	4.1	5.22
CaO	17.3	—	13.4	7.12
MgO	4.7	10.0	3.3	0.19
Na ₂ O	0.6	—	7.9	7.84
K ₂ O	—	—	1.7	3.46
B ₂ O ₃	8.0	—	4.7	6.25
BaO	—	—	0.9	—
SO ₃	—	—	—	—
F ₂	0.1	—	Trace	—
As ₂ O ₅	—	—	—	—
ZnO	—	—	—	1
TiO ₂	—	—	—	Trace

resin grade HSR 8131 was obtained from Bakelite Hylam Ltd, India. The resin was cured using methyl ethyl ketone peroxide and cobalt naphthenate as the curatives, procured locally. With the objective of improving adhesion between the glass fibres and the resin matrix, the glass fibres of each kind were treated with a silane coupling agent (*v*-methacryloxypropyl trimethoxy silane, grade A-174 from Union Carbide, USA) following established procedures [4]. Rods impregnated with resin (containing an appropriate dose of the curatives) of diameter 6.5 ± 0.3 mm were prepared using UR by a hand pultrusion technique employing a Borosil glass tube of appropriate dimension for shaping. The shaped FRP rods were allowed to cure for 72 h at room temperature (35 °C) and finally post-cured in an oven at 100 °C for 4 h. Test pieces of 120 mm length were then cut out from the cured rods. In each case of making composite laminates using N-glass and E-glass CSM, a hand lamination technique was employed taking three layers for each laminate and maintaining a resin to reinforcing fibre weight ratio of nearly 67:33. The curing and post-curing were done in the same way as for making unidirectional composites. The laminates came out with a thickness of 1.3 to 2.0 mm and strips of 80 mm \times 13 mm were cut out for testing purposes.

2.1. Evaluation of properties

Tensile strengths of individual filaments of E- and N-glass rovings and the flexural strengths of the prepared composite rods and reinforced laminates were determined in an Instron 1185 universal testing machine. Specific rods or laminates were also subjected to different degrees of chemical attack separately using 10% HCl, 0.5% NaOH and 10% NaCl solutions over different lengths of time under boiling (refluxing) conditions. The flexural strengths of samples subjected to chemical attack as above and kept under different hydrothermal conditions over different time periods were also measured under the standard conditions of measurement for both E-glass and N-glass fibre-reinforced composite rods and laminates, and the data in each case for the two types of glass fibre reinforced systems (E-glass and N-glass fibres) were then compared.

Hydrothermal ageing of E-glass fibre-reinforced laminates has recently been reported using a non-destructive acousto-ultrasonic technique [5]. The same technique has now been used for evaluation of the strength reduction due to hydrothermal effects for the N-glass laminates. An acoustoultrasonic test equipment (Model 206 AU, AET Corporation, USA) was used for this study. The pulser unit of the equipment injected ultrasonic pulses into the composite test specimens. Each pulse produced simulated stress waves that resembled acoustic emission events. The receiving transducer relayed the signals back to the acoustic emission section for electronic processing. The continuously repeating bursts of simulated stress waves were displayed on the oscilloscope of the display unit.

Each specimen was subjected to measurement of the acousto-ultrasonic stress-wave factor E by placing the receiving transducer at the centre of the specimen. The equipment was set at gain 50 dB, threshold voltage 0.25 V (auto mode operation), pulse rate 2000 s^{-1} , pulse energy 50 V and gate width 187.2 μs , all of which were kept constant for all the measurements. In the stress-wave factor measurement simulated stress waves were repeated at a fixed rate r (2000 s^{-1} in this study), with each successive burst identical to its predecessors. After amplification, the received signals were sent to a counter that registered the number of oscillations, n , in each burst exceeding a fixed threshold voltage. The counter was reset automatically after a predetermined time interval g (1 s in this study) and the previous count was held in a memory and digitally displayed. The displayed count assumed a constant value soon after the probes were placed on the specimen. The number that was displayed, $E = grn$, is defined as the stress wave factor [5].

Ten specimens were tested dry in three-point flexure employing the Instron machine at a displacement rate of 2 mm min^{-1} which was maintained the same for all tests. A large number of test specimens of each kind were kept in distilled water at 100, 80, 60 and 42 °C for hydrothermal degradation. Of these, ten samples of each kind were drawn at random after a specified number of hours of ageing for all water temperatures and they were subjected to stress-wave factor measurements and to flexure tests after cooling to the laboratory temperature (30 °C). The flexural strength was determined following standard procedures and is expressed as an average of ten observations. The stress-wave factor was normalized relative to the maximum E value ($E_{\text{max}} = 698$) found for all specimens, i.e. $N_{\text{swf}} = E/E_{\text{max}} = E/698$. E and N_{swf} are both relative and depend on factors such as probe pressure, signal gain, reset time, threshold voltage and repetition rate. All these factors have been kept constant in this study [5].

3. Results

3.1. Comparison of tensile strength and tensile strength retention of E-glass and N-glass fibre filaments

Tensile strengths (TS) of the initial E- and N-glass fibre filaments after different periods of immersion in boiling water are given in Table II. Retention values (%) of TS after different periods of boiling in water are also computed and given in the table. The initial dry strength of E-glass fibre filaments is substantially higher than that of N-glass fibre filaments. The N-glass fibre filaments, however, show greater resistance to a boiling water environment and it almost reaches a level of tensile strength comparable with that of E-glass fibre after 100 h of boiling in water; thereafter the N-glass fibre filaments show higher TS values than the E-glass fibres, and after about 216 h of boiling in water (see Table II) the N-glass fibre filament retains nearly 75% of its dry strength while the E-glass fibre filament show a retention value of only 50% of its dry strength.

TABLE II Tensile strength and retention of strength of E- and N-glass fibre filaments in boiling water

Time in boiling water (h)	E-glass fibre filament		N-glass fibre filament	
	Tensile strength (MPa)	Percentage retention of strength	Tensile strength (MPa)	Percentage retention of strength
0 (dry fibre)	1408.27	—	1027.56	—
24	1053.58	74.81	976.30	95.01
48	944.87	67.09	944.19	91.88
92	1028.33	73.02	826.53	80.43
96	1000.93	71.07	897.45	87.33
120	705.56	50.10	843.80	82.11
147	763.43	54.21	836.36	81.39
196	724.84	51.47	782.13	76.11
216	702.10	49.85	768.98	74.83

3.2. Resistance of E-and N-glass unidirectional composites in different chemical environments under boiling conditions

After having established that N-glass fibres are more resistant than E-glass fibres in boiling water, it was thought of interest to further examine how differently composites based on them would resist a dilute mineral acid (10% HCl) solution, dilute alkali (0.5% NaOH) solution and salt (10% NaCl) solution each under boiling condition. Comparative results are shown in Figs 1, 2 and 3, respectively. For comparable periods of leaching under boiling condition in each chemical environment, the N-glass fibre-reinforced composite exhibits a flexural strength retention value twice or even more than the retention of flexural strength for the E-glass composite. What is more important is that the E-glass composite suffers a very sharp loss in strength over the initial zone of leaching (the initial rate of fall in strength being $2\% \text{ h}^{-1}$ in acid, $3\% \text{ h}^{-1}$ in alkali and $0.65\% \text{ h}^{-1}$ in salt solution), while over this zone and in fact over the whole zone of leaching the N-glass composite exhibits a relatively slow rate of property loss (the rate of fall in strength being $0.1\% \text{ h}^{-1}$ in acid, $0.3\% \text{ h}^{-1}$ in alkali and $0.1\% \text{ h}^{-1}$ in salt solution).

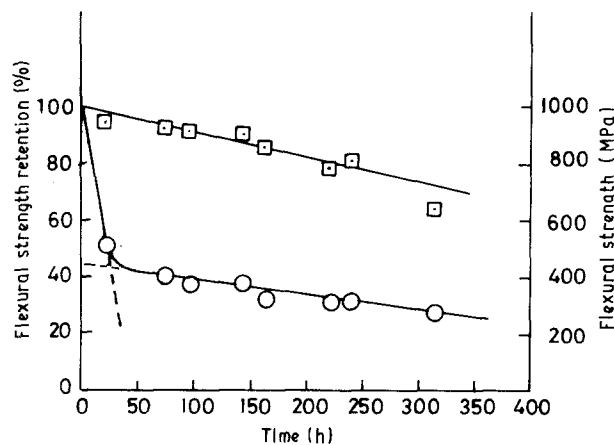


Figure 1 Variation of flexural strength retention of degraded (□) N-glass and (○) E-glass composites with time of degradation in boiling 10% HCl solution. Flexural strengths of initial, unaged composites were 972 and 1036 MPa, respectively.

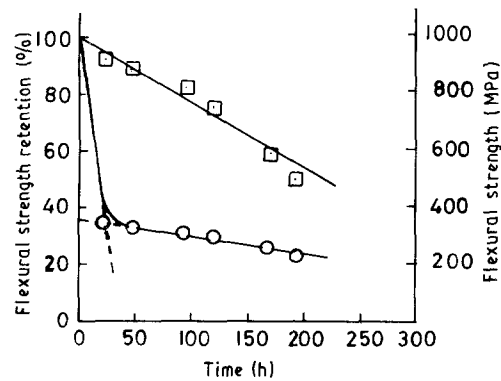


Figure 2 Variation of flexural strength retention of degraded (□) N-glass and (○) E-glass composites with time of degradation in boiling 0.5% NaOH solution. Flexural strengths of initial, unaged composites were 972 and 1036 MPa, respectively.

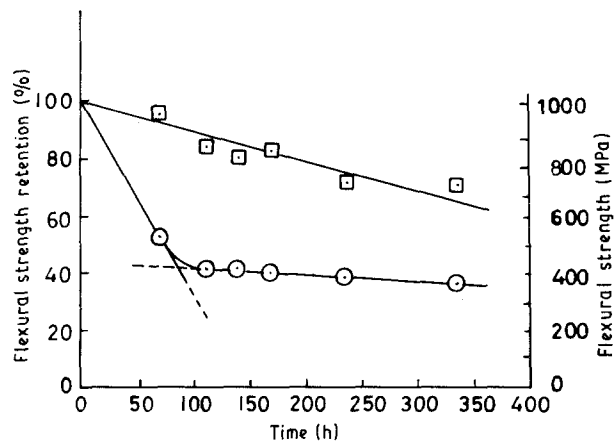


Figure 3 Variation of flexural strength retention of degraded (□) N-glass and (○) E-glass composites with time of degradation in boiling 10% NaCl solution. Flexural strengths of initial, unaged composites were 972 and 1036 MPa, respectively.

3.3. Hydrothermal ageing of N-glass CSM laminate: effect of time and temperature on ageing

Fig. 4 shows plots of average flexural strength (σ) values obtained after different time periods of ageing at 100, 80, 60 and 42 °C against the normal stress wave factors, N_{swf} (Table III). Each plot shows a monotonic increase of σ with N_{swf} . The linear regression curve

TABLE III Flexural strength of N-glass fibre CSM laminates subjected to different extents of hydrothermal degradation at different temperatures in water

Temperature (°C)	Time (h)	Flexural strength		Deviation (%) ^a	Lowest mean stresswave factor, <i>E</i>	<i>N_{swf}</i> ^b
		Average flexural strength (MPa), measured	Flexural strength (MPa), calculated			
100	0	214.89			584.60	0.837
	24	187.55			464.30	0.665
	45	170.02			431.80	0.618
	92	167.80			416.50	0.596
	119	164.16			388.50	0.556
	144	161.26			333.10	0.477
	191	144.39			288.00	0.412
	264	127.55			250.00	0.358
	330	120.91			225.80	0.323
80	0	214.89	214.47	-0.19	584.60	0.837
	24	192.56	188.75	-1.97	482.00	0.690
	47	181.70	182.62	+0.50	457.33	0.655
	120	174.34	179.12	+2.74	443.33	0.635
	167	166.53	168.45	+1.15	400.83	0.574
	190	153.90	156.90	+1.94	354.83	0.508
	60	0	214.89	214.47	-0.19	584.60
24	205.58	196.97	-4.18	514.83	0.737	
96	189.07	186.47	-1.37	473.00	0.677	
167	186.44	180.87	-2.98	450.33	0.645	
264	177.28	169.85	-4.19	406.33	0.582	
336	170.51	165.30	-3.05	383.33	0.556	
42	0	214.89	214.47	-0.19	584.60	0.837
	46	210.93	196.27	-6.95	512.00	0.733
	171	185.81	187.35	+0.82	476.66	0.682
	267	180.96	183.67	+1.49	461.60	0.661
	338	175.93	169.67	-3.55	405.50	0.581
	432	166.68	164.07	-1.56	383.30	0.549
	527	152.62	146.05	-4.30	311.50	0.446

^a Deviation between measured and calculated flexural strength values expressed in % of the measured values.

^b $N_{swf} = E/E_{max} = E/698$.

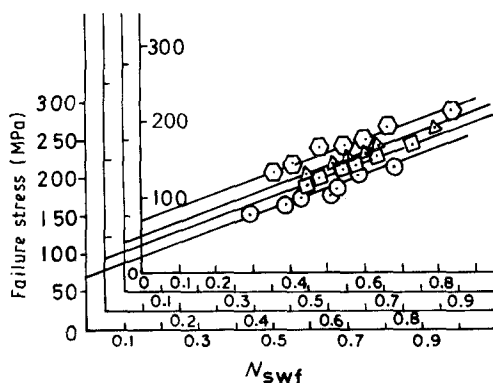


Figure 4 Flexural strength as a function of normalized stress wave factor (*N_{swf}*) for N-glass fibre composites aged in water at (○) 100, (△) 80, (□) 60 and (◇) 42°C.

fitted to the data at 100°C had a coefficient of determination of 0.98 and gave the relation correlating σ and *N_{swf}*:

$$\sigma = 175N_{swf} + 68 \quad (1)$$

The average normalized stress-wave factors at different ageing times at 80, 60 and 42°C were calculated and then the flexural strength values were computed using Equation 1 obtained from the data for degrada-

tion at 100°C. The calculated values as well as those measured at different ageing times along with its percentage deviation from the measured strength are given in Table III. In each case, agreement between the measured and calculated strength values is quite close (within $\pm 4\%$) indicating that Equation 1 is of general applicability. A greater deviation in strength values (10%) was observed for E-glass laminates than for N-glass laminates kept in water at 60°C [5]. A similar comparison of measured and calculated strength values for E-glass and N-glass reinforced (unidirectional) composites, however, showed that the two strength values are quite close, with maximum deviations of about 15 and 5% for E-glass and N-glass composites, respectively.

4. Discussion

In the present study it has been shown that the stabilities of N-glass fibre composites are greater than that of E-glass composites in different chemical environments. On exposure to aqueous acid, alkali and salt solutions under boiling condition the three phase zones of the composites, i.e. the body of the reinforcing fibre, the resin matrix and the fibre-resin interfacial region, are likely to have been affected or attacked,

though not to equal extents. The polyester component of the composite is likely to undergo mild swelling in water which may also mildly plasticize the resin in the absence of inorganic impurities. Thermal treatment and exposure to moisture/water/aqueous chemicals may lead to different degrees of severe undesirable effects such as polymer degradation, fibre-matrix debonding, chemical attack of the fibre surface etc. [6–8]. The strength of N-glass fibre composites shows a higher retention trend than that of E-glass fibre composites on boiling in water for several hours.

A major disadvantage of E-glass is that it is easily attacked by dilute acids. The flexural strength retentions of both E-glass and N-glass fibre (unidirectional)

composites immersed in boiling 10% HCl, 0.5% NaOH and 10% NaCl solutions are shown in Figs 1, 2 and 3, respectively. In a large measure, strength loss of the glass-fibre composites in boiling chemical environments is due to the occurrence of ion-exchange reactions involving replacement of cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Al^{3+} near the surface of the glass by protons. Because the protons are smaller in size than the replaced cations, it is believed that tensile stresses are induced in the surface of the glass and that such stresses can become large enough to promote cracking [9]. Reinforcing fibres from E-type glass having a very high level of CaO , MgO and Al_2O_3 content (Table I) are significantly susceptible to

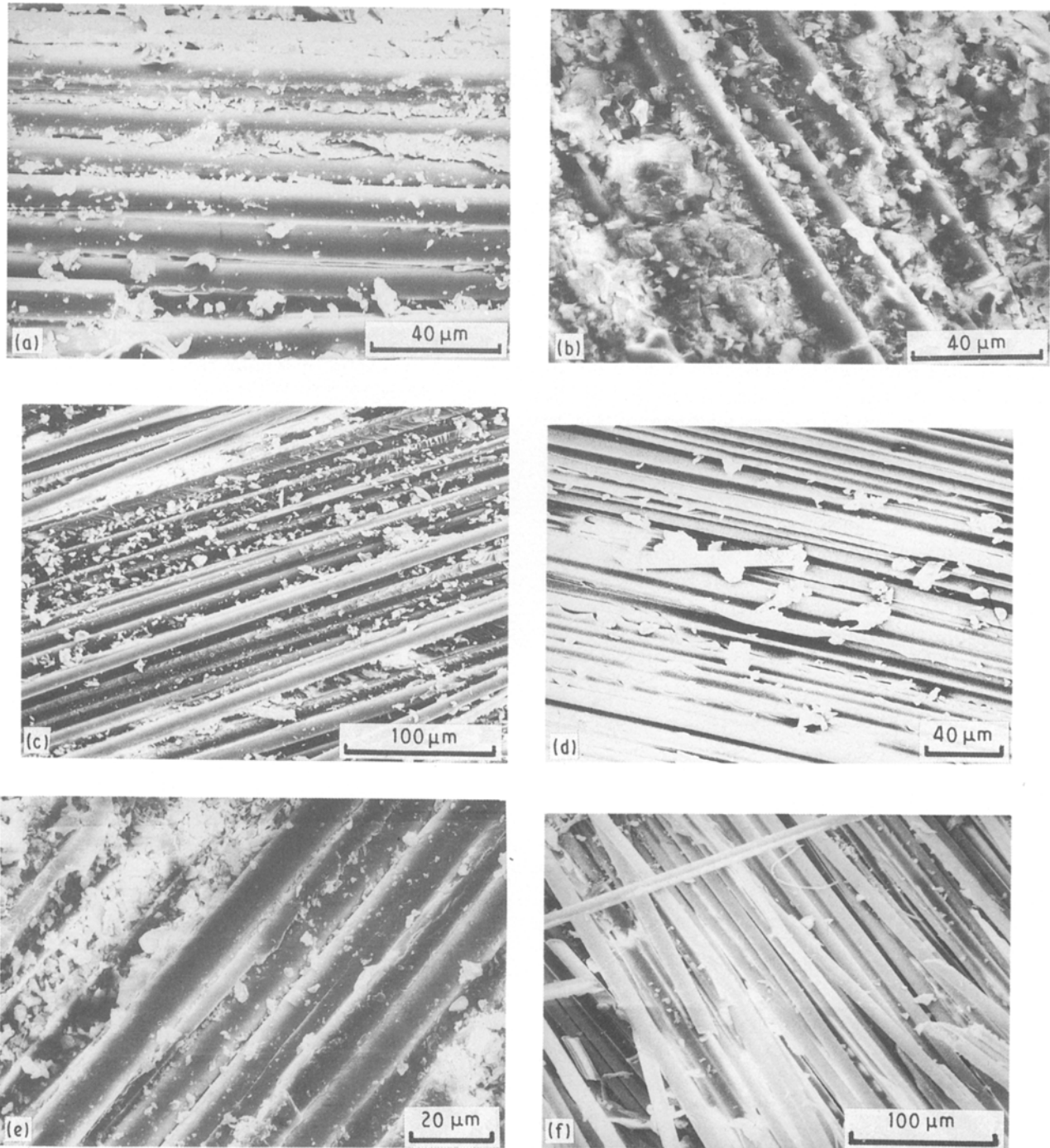


Figure 5 Scanning electron micrographs of unidirectional N-glass and E-glass fibre-reinforced composites. (a) Initial unaged N-glass and (b) initial unaged E-glass; (c) N-glass and (d) E-glass degraded for 24 h in boiling HCl (10%); (e) N-glass and (f) E-glass degraded for 24 h in boiling NaOH (0.5%).

chemical corrosion when exposed to (strongly acidic) aqueous environments [9–11], readily permitting leaching of Ca^{2+} , Mg^{2+} and Al^{3+} ions from the surface. N-glass fibres have about 20–25% lower content of metal oxides such as CaO , MgO and Al_2O_3 and a significant percentage of alkali metal oxides (10–11% higher than in E-glass), and the overall balanced effect is that N-glass fibres or composites reinforced with them suffer much less corrosion and hence much lower strength loss in different aqueous environments in comparison with E-glass fibres or composites based on them.

4.1. Further studies of environmental degradation by scanning electron microscopy

Fig. 5 shows micrographs of N-glass and E-glass fibre-reinforced unidirectional composites and the effects of degradation under boiling condition in 10% HCl and 0.5% NaOH solution in each case, as studied by SEM. In each case the fibres were treated with the silane coupling agent mentioned above and the composites were prepared under comparable conditions, giving a comparable fibre–resin ratio (33:67). Micrographs of initial composites (N-glass reinforced and E-glass reinforced, Fig. 5a and b, respectively) appear more or less comparable in nature, the glass strands being held together by the resin matrix. Treatment with boiling HCl (10%) or NaOH (0.5%) clearly degrades the E-glass fibre-reinforced laminates much more drastically than the N-glass laminates, as revealed by the corresponding scanning electron micrographs (Fig. 5c and d and Fig. 5e and f, respectively), the debonding of the glass strands being very severe in the case of E-glass composites. This would therefore expectedly lead to a drastic fall in the flexural strength of the E-glass fibre-based composites on exposure to the degradative effects of aqueous acid and alkali. The results of the SEM studies therefore support the results of the strength analysis for evaluation of the

comparative stabilities of composites based on E-glass and N-glass fibres in different chemical environments. Thus, N-glass fibre-based composites are more stable than the E-glass fibre-based composites under different chemical environments.

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