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Some hygrothermal effects on the mechanical behaviour and fractography of glass–epoxy composites with modified interface

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The mechanical behaviour of glass fibre-reinforced epoxy composites with introduced layers of materials and with fibre coating is studied. The role of aerosil powder as a filler material is investigated, and the fracture mode is analysed by scanning electron microscopy. The investigation shows a considerable drop in interlaminar shear stress for the higher fibre volume fraction, whereas the introduction of filler materials to the composite causes no change. Surface mat-reinforced samples show a marginal increase in shear stress. Exposure to moisture reduces the interlaminar shear stress value faster for the higher fibre volume fraction, thereby highlighting the role of the interfacial area. Impact values for coated and uncoated fibres show an identical trend with exposure to dry heat, the former always recording lower values. The impact value decreases faster with moisture absorption for the composite with the higher fibre content. Fractography reveals poor adhesion in the coated laminates.

1. Introduction

The rate at which water is absorbed by a composite depends on many variables, including fibre type, matrix and temperature, the difference in water concentration within the composite, environment, and whether the absorbed water reacts chemically with the matrix. For structural applications, most of the environmental degradation in the composites is caused by a combination of temperature and moisture [1]. The moisture absorbed not only plasticizes the matrix resin, but also changes the state of stress in favour of cracking through swelling [2]. At the fibre/matrix interface, moisture may reduce the bond strength by breaking bonds, as in glass/epoxy composites [3].

Wright [4] has observed that both the rate of water pick-up and the total amount of moisture absorbed depend on the chemical structure of resin and cross-linking agent, together with temperature and relative humidity. Absorbed moisture causes dimensional changes and generates internal stresses. The subject of moisture absorption has thus engaged the attention of many workers.

The present work considers the hygroscopic and dry heat effects on mechanical properties. An effort to correlate the mode of fracture with mechanical test data has also been made. It is natural to expect that environmental effects of moisture, liquid used (jet fuel, aviation oil, salt solution, etc.) and dry heat will affect the interface regions which form the boundary between fibre and resin. In this work, a preliminary attempt has been made to understand the effect of introducing additional layers at the glass–epoxy interface on the mechanical properties. We also consider the introduction of filler material to the resinous matrix.

2. Experimental procedure

A 0.25 mm plain-weave epoxy-glass fabric with a density of 2.54 $g\,cm^{-3}$ was used. The fabric had an epoxy compatible finish and was coated with a silane-coupling agent. Composite laminates of 3 mm thickness were made using a LY556/HY951 resin hardener system supplied by Ciba Giegy Ltd, Hindustan. Laminates of the same thickness but containing different volume fractions of fibres were made using the modified compression moulding technique.

2.1. Modified compression moulding (MCM)

Compression-moulded samples are considered to be inferior to those fabricated in the autoclave because of non-uniform resin distribution. To improve the distribution of resins, a modification in the processing route was introduced and found to give better results. Details are given below.

A schematic diagram of the moulding unit is given in Fig. 1. The bottom plate of the mould was covered with a teflon film for easy separation of the laminate after curing. On the bottom plate, glass fabric pieces cut to the desired size of 300 × 225 mm were laid one by one after impregnating with the resin, hardener and

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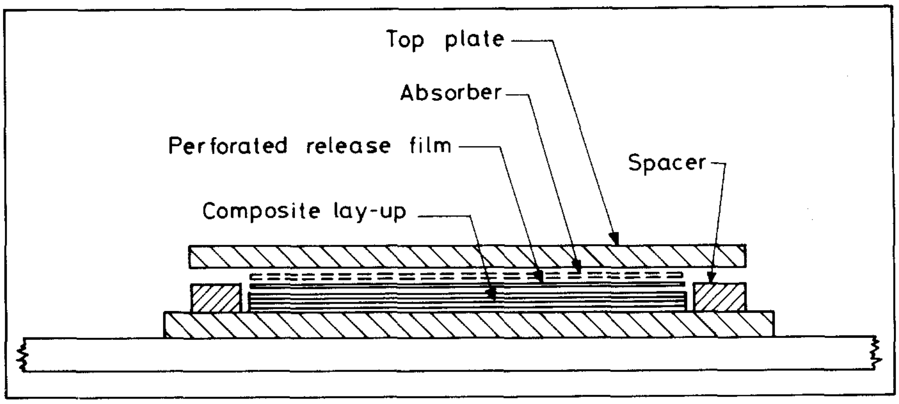

Figure 1 A schematic diagram of the modified compression-moulding set-up.

diluent mix. After stacking the resin-coated layers, a perforated nylon film was placed over the lay-up. This acts as a release film between the breather material and the laminate, and simultaneously provides a path for the absorption of excess resin by the breather. Over the perforated film, two to four layers of surface mat followed by zero to five layers of jute cloth were stacked to absorb the squeezed-out excess resin. 3-mm thick aluminium spacers were placed along the peripheral edges of the lay-up so that it was within the area enclosed by the spacers, while the porous film and breather material rested over the lay-up and the spacers. Finally the top plate, which is also finished with a teflon film, was placed on the lay-up and the breather stacked thus. The mould was then placed under a hydraulic press and a suitable compaction pressure applied till the top plate touched the spacers. The lay-up was allowed to cure under pressure for 20 h.

2.2. Fabrication of laminates

Normal laminates of two different volume fractions were made using 10- and 16-ply glass fabric. As the test condition requires the use of 3-mm thick samples, the procedure employed for making the laminates as well as the pressure employed during compaction are obviously different for the two different glass-fabric contents. In the 10-ply sample, a mixture of LY556 resin and 10% hardener HY951 was employed. For the case of 16-ply laminates, in addition to the above, a diluent (Dy 026) was used for greater flow of resin during compaction. The pressure used in this case was $100\ \mathrm{kg\,cm^{-2}}$ while the 10-ply laminates were made under pressure of $50\ \mathrm{kg\,cm^{-2}}$.

In this investigation the possible roles played by additional layers of different materials at the interface forming the glass and resin system were examined. Thus in one case a surface mat, normally used to attain better surface finish, was tried. (The surface mat is a glass tissue, sprayed with starch and passed through callendering to maintain a fine thickness, which is generally used in glass–epoxy and polyester composites for a glossy, resin-rich surface). In the second case the glass fabric was coated with polyvinyl alcohol (PVA) which is known for its self-releasing characteristics. In the third and final set aerosil powder (2 wt %) was used as the filler material mixed in the resinous matrix; these experiments were conducted on laminates containing 10-ply fabric.

2.3. Specimen preparation

Short-beam test specimens for determining interlaminar shear stress (ILSS) were cut according to the ASTM specification [5] which requires a depth-to-span length of 1:5, and a depth-to-length ratio of 1:7. The specimen geometry was $21 \times 10 \times 3$ mm. Izod impact-test specimens (63.5 mm long and 10.2 mm wide) were made, again using the ASTM standard [6] to determine the impact resistance of the composite. Notches were not made for the present tests.

For moisture-absorption studies, the edges were coated with an impermeable resin film to avoid moisture penetration, following the work of Romenenkov and Machavariani [7]. The procedure involved drying the samples, applying a thin layer of resin along the edges, drying the samples and exposing them to moisture by immersing in distilled water at room temperature. The exposed samples were used for impact and ILSS tests.

For dry heat studies, an oven was employed: composite test samples of the desired geometry were placed inside the oven, and removed at varying time intervals for evaluation of short beam and izod impact studies.

3. Results and discussion

3.1. Interlaminar shear strength

The composites with the interface reinforced by surface mat material showed nearly 10% increase in ILSS value over the normal laminate (Table I). Further, it is obvious from the same data that the composite strength with PVA coating shows a fall of 35%. However, the resinous matrix composite containing aerosil filler material showed no significant change in ILSS. The probable cause of the increase in ILSS of the reinforced interface composite is some kind of knitting of the adjacent plies by the fine fibrils in surface mat, making the shearing process difficult. Referring to Fig. 2, it is apparent that the layer of the

TABLE I Interlaminar shear stress and impact values of laminates

Type of laminate	ILSS (MPa)	Impact values (J)
1. Normal laminate	31.4	1.9
2. Reinforced with surface mat	33.9	2.2
3. Coated with PVA	20.2	1.7
4. Matrix with aerosil (2%) as filler material	31.6	1.7

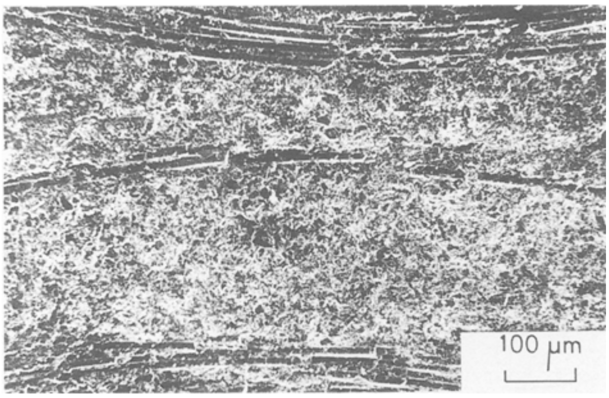

Figure 2 Micrograph illustrating a layer of glass surrounded by resinous matrix.

surface mat is sandwiched well between the resinous surrounding. Fig. 3 illustrates the cusp features observed in the sample, indicating the occurrence of a shear process in the material.

The distinct fall in ILSS in the case of the coated interface can be ascribed to the weakening of bonding between the fabric and the resin. This explanation is supported by observations made under the SEM and shown in Fig. 4, where due to the PVA coating the poor interface bonding is amply demonstrated. Furthermore, some fragmented fibres spread over the matrix can be distinctly seen. All this emphatically suggests the presence of a weak region in the composite laminate due to a deliberately adopted processing route. That very little adhesion of the resin to the fibre occurs in this system is demonstrated in Fig. 5. A comparison of micrographs of samples with and without aerosil powder filling (Fig. 6a and b) shows a similarity of features. The ILSS values for these two cases are nearly the same.

Coming to the effect of environment on ILSS in the four types of laminates, it is obvious that exposure up to about 200 h to dry heat has a marginal influence (Fig. 7). Either they show a saturation trend when exposed for a long period, or they show a small increment, depending on the type of layers used for the test case. This increment is possibly due to a post-cure process that takes the laminates close to complete-cure conditions during such exposure, leading to the attendent rise in ILSS values. However amongst the composites investigated the fibres coated with PVA show the lowest ILSS values, thereby reinforcing the explanation offered above, namely that coating of this nature weakens the interface. Due to the wettability

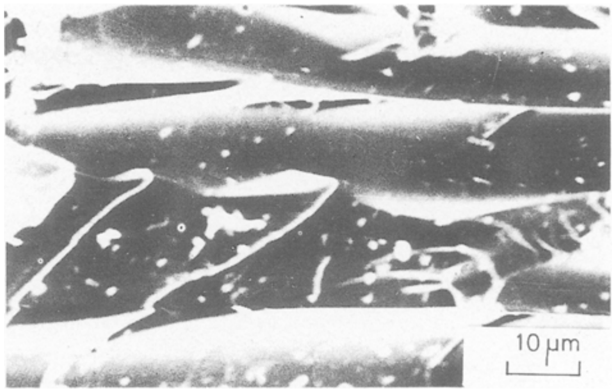

Figure 3 Cusp features seen in the sample containing a layer of glass wool.

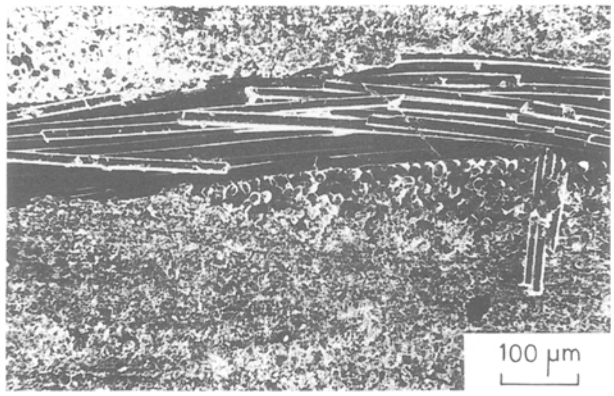

Figure 4 A composite showing poor interface bonding between the PVA-coated glass fibre and the resin.

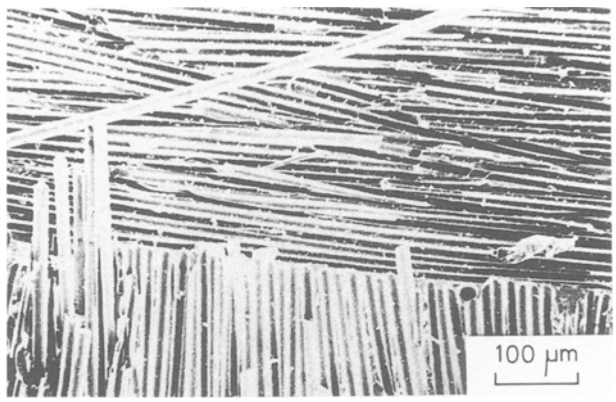

Figure 5 A reinforcement-rich area of the composite showing a little adhesion of the resin to the fibre.

condition between PVA and the matrix resin as well as that between PVA and the fibres being poor, the interlaminar failure process is further assisted.

A small but interesting rise in the trend after a long exposure is noticed in laminates with aerosil powder. The loss of initial moisture and other volatiles could have contributed to this trend.

ILSS data with increasing times for absorption of moisture are presented for two different fibre volume fractions in Fig. 8. It is observed that the degradation is rapid when the fibre volume fraction is large (or the

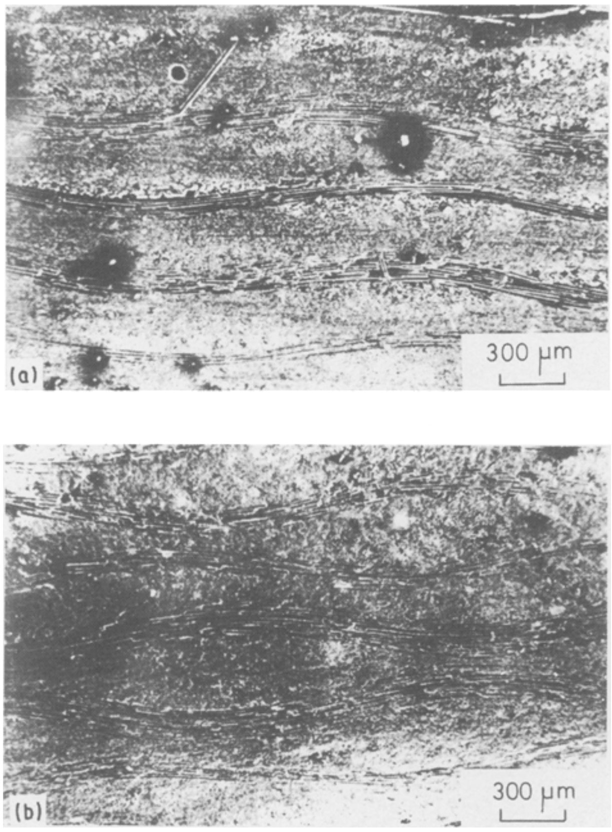

Figure 6 Micrographs of (a) aerosil powder-particle filled and (b) normal laminates.

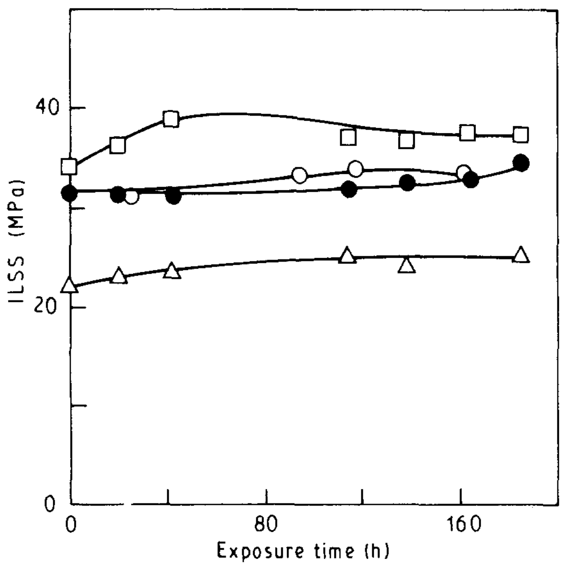

Figure 7 The variation of interlaminar shear strength with time of exposure during dry heat tests. Laminates with □, glass wool; ●, particle-filled matrix; △, PVA coating; ○, normal laminate.

resin fraction is lower), and the attendent interfacial area is greater.

The fracture features of some of these materials are shown below. Fig. 9 shows normal laminates without filler material, depicting a failure in the matrix region. Curvilinear branching of the cracks is apparent. PVA coating, on the other hand, leaves a cleaner fibre, as seen in Fig. 10. That a stepped appearance occurs in the failure of these materials is obvious from Fig. 11.

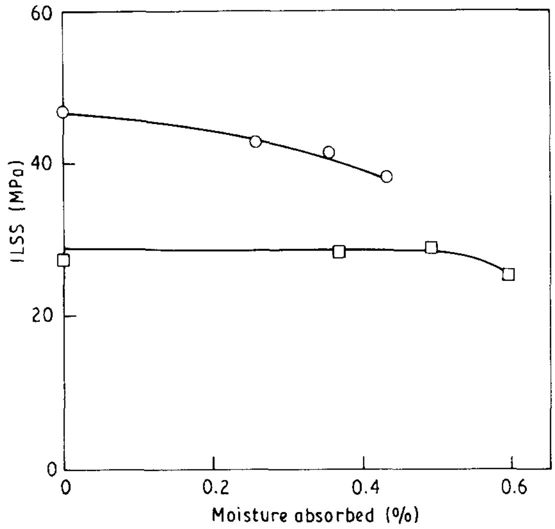

Figure 8 Variation of interlaminar shear strength with percentage moisture absorbed for ○, 16-ply ($V_f = 0.6$); □, 10-ply ($V_f = 0.4$) laminates.

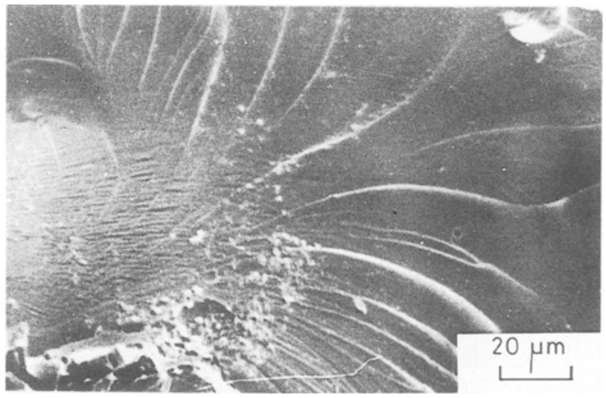

Figure 9 Failure features in resin-rich regions of the normal laminates.

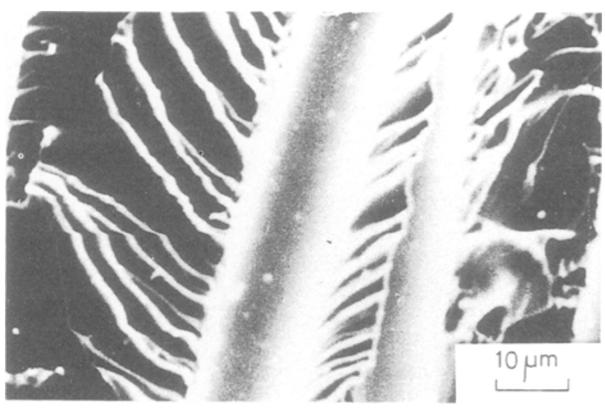

Figure 10 A fibre surface of a PVA-coated failed sample showing hardly any smearing of resinous material.

Aerosil powder shows a river pattern, with a very fine parallel fringe pattern between two major paths (indicated by an arrow in Fig. 12).

3.2. Impact testing

Table I summarises the effect of reinforcement and

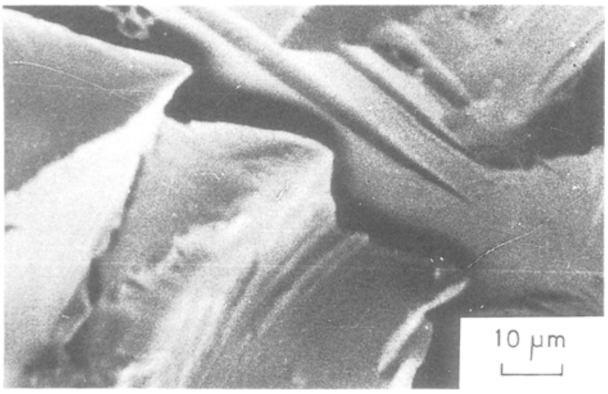

Figure 11 Step-like features in resin-rich areas of the composites.

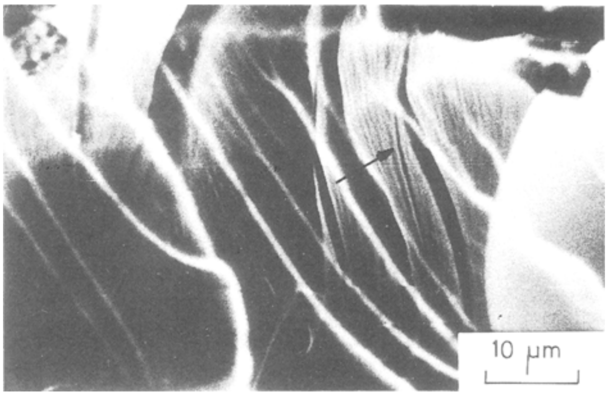

Figure 12 Micrograph showing river patterns. Faint fringe-like features in the top right portion can be seen.

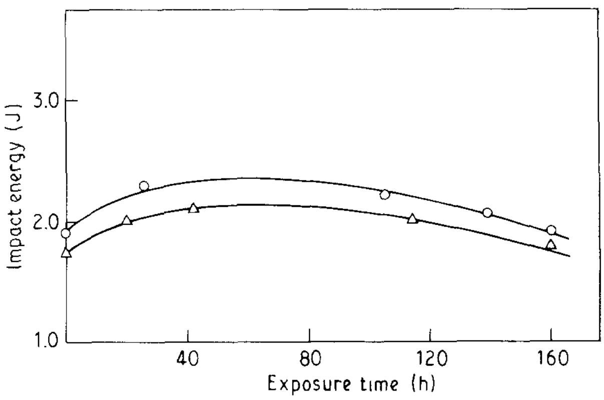

Figure 13 Impact energy variation with time of exposure during dry heat tests. ○, Normal; △, PVA-coated laminates.

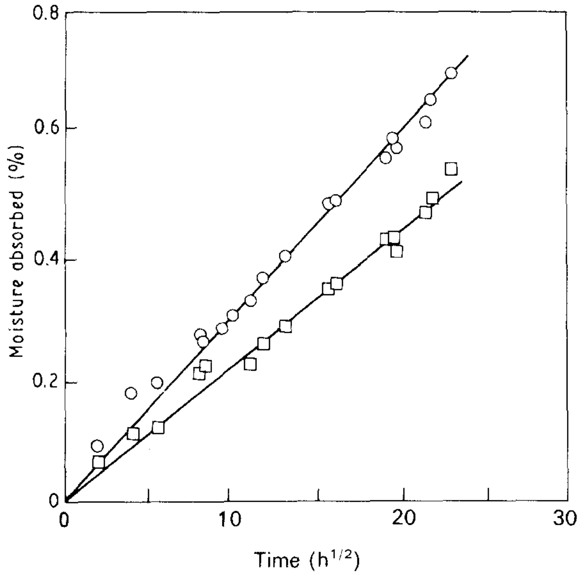

Figure 14 The relationship between percentage moisture absorbed and time of exposure ($t^{1/2}$) for laminates containing ○, 40; □, 59% volume of fibres.

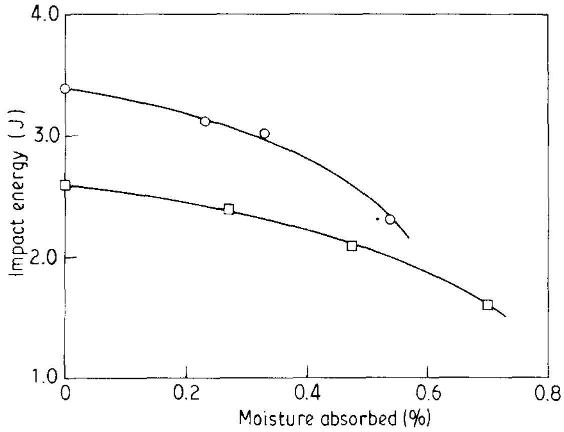

Figure 15 Impact energy variation with percentage moisture absorbed for two laminates. V_f = ○, 60%; □, 40%.

filler material on impact values. Reinforcement results in an improvement in the impact resistance values (~16%). A 13% fall was observed in the case of composites with a PVA-coated interface. For aerosil-filled composites, the data showed a decrease of about 13%.

In the dry heat test (50 °C) the impact data of the normal laminate showed an initial increase of 20% during the first 25 h of exposure time, beyond which the values decreased (Fig. 13). Similarly the laminate with a coated surface also showed an increase (24%) in the first 40 h of exposure, following which a decrease was noted. These results support the earlier contention that post-curing effects are responsible for the rise in impact resistance, as the dry heat experiments are conducted at elevated temperatures. It was noted during the experimentation that a definite trend for impact value variation with exposure time could not be established for the laminates having either a filler material in the matrix or an interface reinforced with glass wool. If the early rise is due to the polymerization process approaching completion, the subsequent drop could be caused by the exhaling of water vapour or by volatiles giving rise to a brittle laminate, which will predominate over the other thermal processes occurring at longer time intervals.

The present results in MCM-type normal laminates show a Fickian behaviour for moisture absorption in both 59% and 40% fibre volume-containing composites (Fig. 14). It is interesting to note that composites having lower amounts of fibre exhibit higher absorption. Finally, both the lower fibre volume-containing composite and the higher one show a decreasing impact resistance with moisture absorption. The rate at which the impact value is lowered due

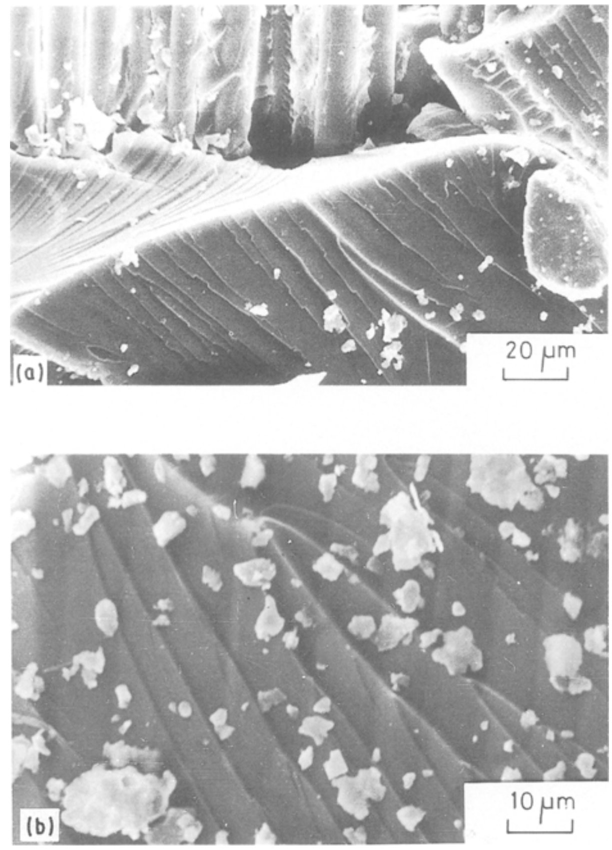

Figure 16 Micrograph showing river patterns in normal laminates. Note (a) resin adherence to fibres and (b) fragmented particles distributed on the matrix due to impact loading.

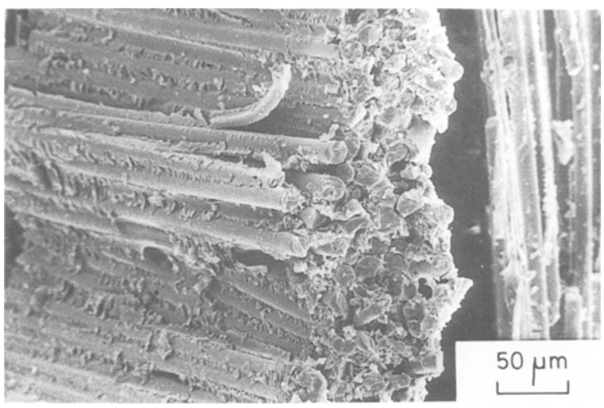

Figure 17 Another region of the sample in Fig. 16 showing a bundle of fibres with considerable resin adherence.

to moisture is greater in the higher fibre volume-bearing composite, as indicated in Fig. 15. This can be due to a thinner resin layer existing at higher fibre fractions.

Finally, the fracture features of normal laminates, and those with PVA coating following failure due to impact loading are discussed. The normal laminates show good river patterns in the resin-rich regions (Fig. 16a and b) and considerable resin adherence to the fibre (Fig. 17). PVA coating, on the other hand, shows cleaner fibres (Fig. 18a) and considerable ripple formation in the resin-rich areas (Fig. 18b). The poor resin adherence in this type of coated laminate, as well

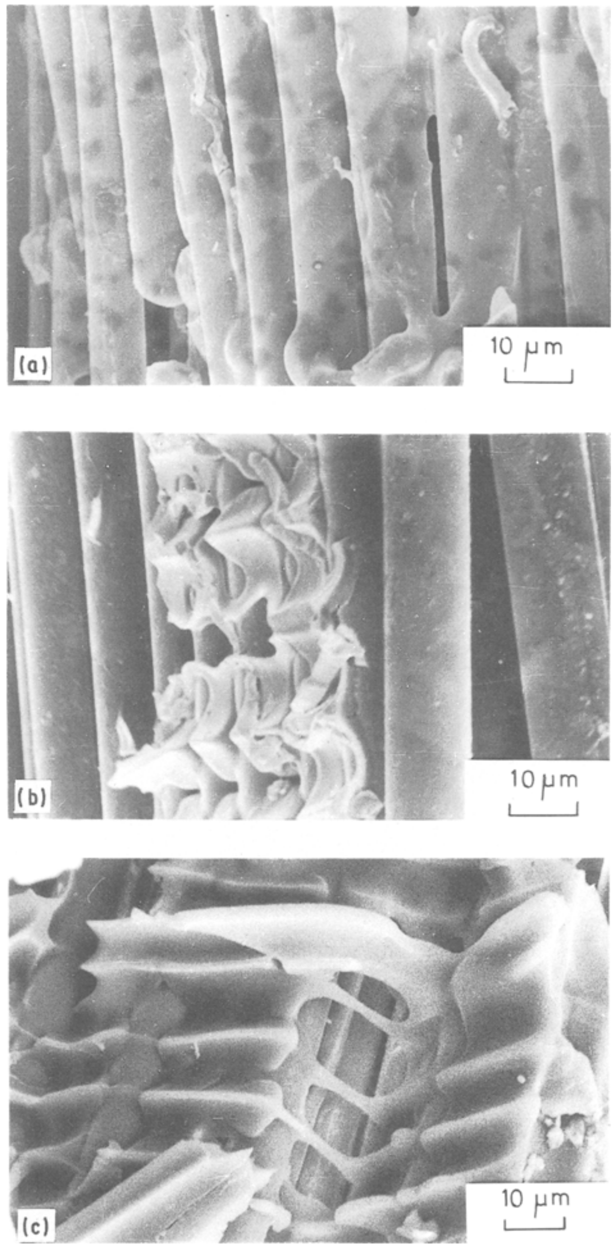

Figure 18 PVA-coated sample showing (a) poor resin adherence to the fibres; (b) rippled features in the resinous medium; (c) features resembling rib formation.

as the fast propagation of cracks denoted by the ripple formation, is responsible for the lower impact values recorded in Table I. The extensive rib formation in PVA-coated samples is depicted in Fig. 18c. Thus the mode of failure in the normal and the PVA-coated composite laminate is not the same.

4. Conclusions

1. Moisture absorption brings down the ILSS values as well as the impact resistance. The effect is more pronounced in laminates containing a higher proportion of fibres. The impact values of dry heat-exposed samples show a similar trend for the coated and uncoated composites, the latter yielding higher values.

2. Exposure to dry heat either has a negligible effect or shows a perceptible increase, depending on whether

filler material or a layer of glass wool at the interface is used. Coated fibres show a poorer response with exposure to dry heat.

3. Fractography reveals a considerable difference in matrix surface features.

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