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Transverse moisture sensitivity of aramid/epoxy composites

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Transverse tensile properties of Kevlar 49 aramid/Fiberite 934 epoxy composites have been measured as a function of moisture content. Moisture effects are substantial: losses of 14% in stiffness, 35% in strength and 27% in elongation were observed at 25° C. These losses were caused by the expected degradation mechanisms of matrix plasticization and interface weakening and also by an unexpected mechanism which altered the filaments at higher moisture contents. The filaments appear to become more radially compliant with the introduction of moisture and tend to crack internally. This behaviour may be caused by the moisture interrupting what hydrogen bonding is initially present in the filament defect structure.

1. Introduction

When composites are employed in primary structures, environmental effects that reduce material performance must be considered. Moisture, especially in parts subjected to transient heating, substantially degrades the mechanical response of polymer–matrix composites [1, 2]. Two possible mechanisms have been suggested by which moisture affects most composite systems – matrix plasticization [3, 4] or degradation of the filament–matrix interface [5, 6].

Data available in the literature indicate that aramid-reinforced composites may be particularly sensitive to moisture for several reasons: (1) the filament–matrix bond is weak in the dry condition [7–9]; (2) moisture may diffuse preferentially along the interface [10]; and, (3) unlike most reinforcements, aramid filaments are hygroscopic [10–14]. These results suggest that moisture may weaken the filament–matrix bond, and that it may also alter filament properties.

Moisture is absorbed into Kevlar aramid filaments (E. I. DuPont de Nemours & Co) through an extensive internal defect structure consisting of a partially interconnected network of microvoids and cracks [14]. It is known that absorbed moisture has little effect on the tensile properties of the filament [13, 15], or the composite [16]. There are few data, however, on the effects of moisture on compression, shear or transverse tensile properties. These loadings are sensitive to filament defects, and may also be sensitive to moisture content. Flexural strength, which is determined by compressive buckling in Kevlar/epoxy, has been shown to be a strong function of moisture content [17]. Moisture may aid the buckling of polymer chains into defects by interrupting hydrogen bonds in those regions. Such a mechanism would also affect shear and transverse tensile properties.

This study was undertaken to examine how moisture affects transverse tensile properties of a unidirectional Kevlar/epoxy composite. 90° tensile tests were run at 25° C on specimens equilibrated to various moisture contents between dry and saturated (5.3%). Results show that moisture effects are substantial: losses of 14% in stiffness, 35% in strength, and 27% in elongation were observed at saturation compared to the dry condition. The stiffness reduction seems to indicate that the Kevlar 49 filaments become more radially compliant with the introduction of moisture. At low moisture contents, microscopic analysis revealed that the expected matrix plasticization and interface degradation mechanisms did occur. At higher moisture contents, an additional degradation mechanism – filament splitting – was

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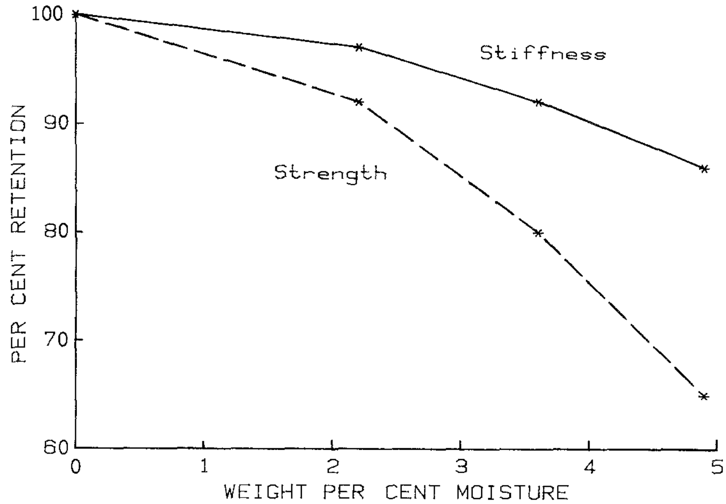

Figure 1 Transverse strength and stiffness retention of Kevlar 49/934 as a function of equilibrium moisture content at 25° C.

observed, and the failure mode changed to a combination of interface and filament splitting. The split filament texture correlates with the filament internal defect spacing. Moisture apparently interrupts what hydrogen bonding is present in the defect regions, and that allows internal filament cracking.

2. Experimental details

Specimens for this study were taken from 10 mm thick unidirectional plates of Kevlar 49/Fiberite 934 epoxy which were supplied by the Army Mechanics and Materials Research Center, Watertown, Mass. The plates were autoclave moulded to a final cure temperature of 150° C and stored in a controlled 50% relative humidity environment. Filament volume fraction was nominally 64% with less than 0.5% voids. Details of the prepreg resin characterization and composite fabrication procedure are given by Roylance [16].

The specimens were diamond-ground with sacrificial aluminium plates on both sides of the composite. Final specimen dimensions were 25 mm wide by 125 mm long by the as-moulded thickness. Despite the aluminium restraint plates, a lip of deformed material formed on the edges of the composite specimens during the grinding operation. To investigate the effect of further machining on specimen properties, half of the specimens were sanded to remove the lip and half were tested as-ground.

Prior to testing, the specimens were equilibrated with one of four environments – dry, 50% and 75% relative humidity, or immersion in 80° C distilled water. Those conditions resulted respectively in 0, 2.2, 3.75, 5.3 wt% absorbed moisture in the Kevlar/epoxy specimens.

Aluminium end tabs were then bonded to the specimens with a room temperature cured epoxy. Testing was performed on a universal Instron testing machine at a cross-head speed of 1.3 mm min^{-1}. Elongation was monitored with a 25 mm, 1% strain gauge extensometer. All tests were run at 25° C and 50% relative humidity. Exposure time to the laboratory atmosphere was approximately 10 min prior to failure. Seventeen specimens were tested in the dry condition. Ten specimens were tested at each of the various moisture levels.

3. Results and discussion

Sanding of the ground specimen edges did not affect measured properties, so average values are reported. Stress–strain behaviour of all specimens was virtually linear. For all exposures, a slight offset in strain was noted at about two-thirds of the ultimate specimen strength; however, the resultant increase in strain was slight. Young's moduli varied from 5.2 GPa (± 0.2 GPA S.D.) in the dry condition to 4.4 GPa (± 0.3 GPa S.D.) with 5.3 wt% moisture. Ultimate strengths ranged from 19.65 ± 2.28 MPa dry to 12.76 ± 1.38 MPa with 5.3 wt% moisture. Corresponding elongations dropped 27% from 0.41% to 0.30%. Retained strength and stiffness as a function of moisture is given in Fig. 1. The 14% reduction in transverse stiffness seen in Kevlar 49/epoxy is roughly twice that observed in graphite/epoxy with similar resin matrices [18, 19]. It is also twice what a micromechanics analysis such as the Halpin–Tsai

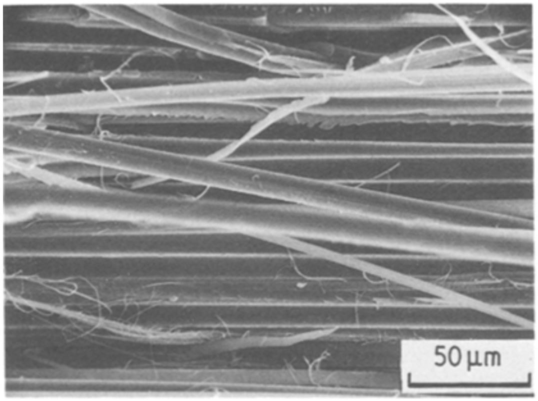

Figure 2 Transverse fracture appearance of Kevlar 49/934 composite in the dry condition.

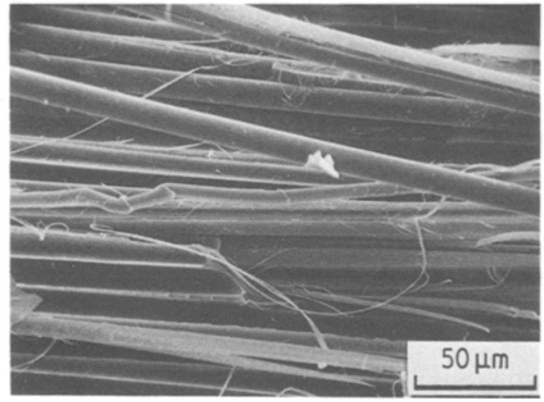

Figure 3 Transverse fracture surface of Kevlar 49/934 with 3.75% moisture showing the beginnings of filament splitting (upper right).

equations [20] would predict with the saturated resin stiffness value from the work of Roylance. The transverse stiffness loss of Kevlar 49/epoxy, which is larger than that from matrix plasticization alone, indicates that some component of the system besides the epoxy matrix is changing. We propose that the interface or the Kevlar filaments themselves (radially) are becoming more compliant in the presence of moisture.

The 35% loss in transverse tensile strength (Fig. 1) shows that it is also quite sensitive to moisture content. Observation of the specimen fracture surfaces in the scanning electron microscope revealed that the strength losses were accompanied by a failure mode change. Failure of the dry Kevlar/934 specimens began in the interface region. The dry fracture surfaces are principally bare intact filaments, although a small amount of resin adhered to the filaments, and some filament splitting could also be found. A representative dry fracture area is shown in Fig. 2.

At 2.2 wt% moisture (50% relative humidity exposure), the failure surface is still characterized by bare filaments, but more resin is present and torn filament skins also appear. It is likely that moisture plasticization toughens the epoxy, and that reduces the amount released from the surface.

With 3.75 wt% moisture (75% relative humidity), even more resin could be seen in the fracture zone. Large internal cracks (upper portion of Fig. 3) also appeared in some filaments. Torn filament skins over extensive distances were also evident. A portion of a torn skin may be seen in the central portion of Fig. 3.

At saturation moisture contents (5.3 wt%), the fracture surface reveals axially split filaments and torn filament skins together with bare filaments and resin. These features are evident in Fig. 4a and b. A higher magnification view of the split filament texture of Fig. 4b is shown in Fig. 5. The internal texture of the wet filament fracture (Fig. 5) is not the fibrillated appearance typical of dry Kevlar transverse failure [21].

The brittle, hackled appearance shown in Fig. 5 resembles the defect network structure shown by Dobb *et al.* [14]. A similar brittle failure surface has also been seen on filaments which have buckled in compression prior to failing in tension [22, 23]. It appears that moisture facilitates internal filament cracking through the pre-existing defect network. The mechanism of moisture interaction within the defect structure is not clear; however, it is reasonable to assume that moisture may be interrrupting what interfibril hydrogen bonding is present in those areas. Moisture also appears to reduce the filament skin–core bonding, and that allows the skins to be pulled away from the core. Thus, when either the filament internal strength or skin–core strength falls below the interfacial tensile strength, a failure mode change to filament splitting occurs.

Transverse tensile failure of Kevlar/epoxy composites is a complex process that involves all the composite phases separately, because moisture interacts with each phase individually. Failure modes are determined by the relative strengths of the phases at a given moisture content. Filament–matrix interface strength seems to control composite strength at low moisture contents, while a mixed interface–filament splitting mode occurs at higher moisture contents. If the proposed degra-

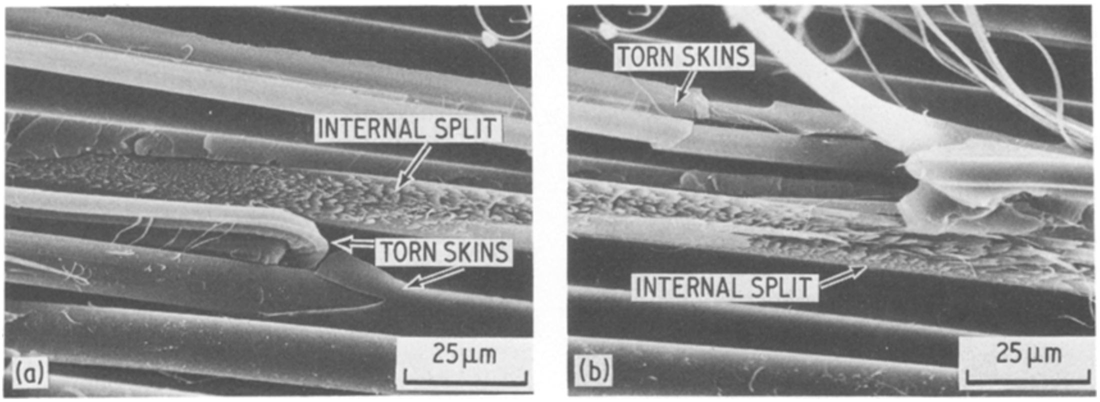

Figure 4 Transverse fracture with 5.3% moisture showing split filaments and skin–core failure.

dation mechanisms are correct, moisture-induced losses may be expected to increase at higher temperatures.

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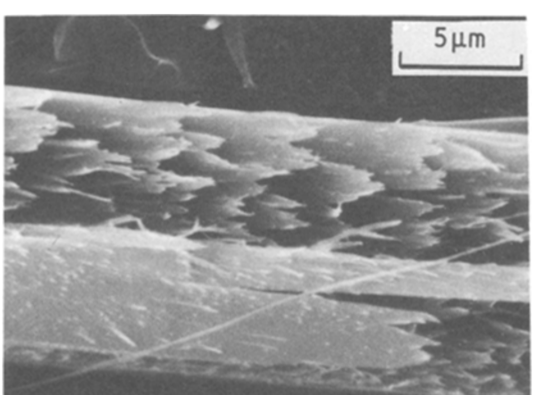

Figure 5 Texture of longitudinally split filament seen in Fig. 4b.

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