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EFFECT OF WATER-BEARING FIBER IN KEVLAR 49-EPOXY COMPOSITES

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Marvin Moss

ABSTRACT

Water has been observed to be adsorbed, and possibly absorbed, by desiccated Kevlar 49 fiber to 6% of the fiber weight in 100% relative humidity. The effect of the water on the transverse flexural strength and elastic modulus of an aliphatic amine-cured epoxy, unidirectionally reinforced with saturated Kevlar 49, has been determined. Such composites are weaker than those made with fiber equilibrated to 0% relative humidity, and the effect persists after a 75°C, 16-h postcure. It is suggested that glycol formation and a consequent excess of curing agent, resulting from a water-resin reaction at the fiber-matrix interface, accounts for the weakening.

INTRODUCTION

Du Pont recommends that Kevlar 49 be oven-dried before it is incorporated into anhydride-cured epoxies, because it has an affinity for atmospheric moisture.[1] Du Pont points out that the reaction between water and the constituents of such epoxies can decrease composite mechanical properties, especially interlaminar shear strength. Although Du Pont results indicate no sensitivity of amine- and dicyandiamide-cured epoxies to moisture, an experiment was undertaken to examine amine-cured epoxies reinforced with Kevlar 49 in two conditions; desiccated and equilibrated to 100% relative humidity, in order to maximize possible effects of the water. A test which is strongly affected by matrix properties is a tensile test transverse to the fibers of an undirectional composite.[2]

Water introduced into an epoxy system before curing is complete produces glycols[3] which inhibit resin polymerization. The competition between the water and the curing agent for the resin would leave unreacted curing agent within the epoxy. Such a condition at the fiber-matrix interface would result in a poor bond. Aspects of moisture penetration and damage have been examined in other composites, but in connection with water introduced after curing.[4-11]

EXPERIMENT AND RESULTS

Water Take-Up

Moisture gain and loss for 370-mg samples of fiber were measured as a function of time, under various relative humidities, preliminary to the treatment of kilogram quantities of the fiber to be incorporated into epoxy. All fiber (milligram as well as kilogram quantities) was baked at 127°C for 25 hr in air as an initial step; this removed most of the water. The small samples were kept in sealed, desiccator-type jars at room temperature in which percent relative humidities (%RH) of 0, 52, and 100 were maintained by means of silica gel desiccant, a saturated solution of sodium dichromate, and plain water, respectively. At specific time intervals, samples were removed and quickly (≈ 30 sec) weighed on a microbalance. After complete saturation had been attained, the wet fibers were transferred to the 0-%RH jar, the dry fibers to the 52- and 100-%RH jars, and the weighing procedure repeated. Dry fibers were also observed with an optical microscope as they extracted water from saturated air in a closed, glass-covered cell.

Once the kinetics of water gain by the small samples had been established, as-received fiber was loosely respooled onto two aluminum tubes, baked, and placed in sealed jars containing pans of either desiccant or water. Equilibration of the spools to the atmospheres in the jars took longer than for the small samples, and was determined by repeated weighing.

The 370-mg samples of oven-dried Kevlar 49 lost 0.6% of their weight when placed in a desiccated atmosphere at room temperature. The fiber then gained 6% of its dry weight when transferred to 100-RH% air; the gain was 50% complete in 6 h, and complete in 100 h (Fig. 1). When replaced in dry air, the fiber lost water at approximately the same rate as it gained it. Dry fiber gained a maximum of 3.4% of its weight in water at 52%RH (curve not shown). Under the microscope, beads of water could be seen forming on dry fiber in a saturated atmosphere in minutes.

The spooled Kevlar 49 took longer (approximately 10 days) to equilibrate to 100%RH, and a maximum weight gain of 5.6% was achieved.

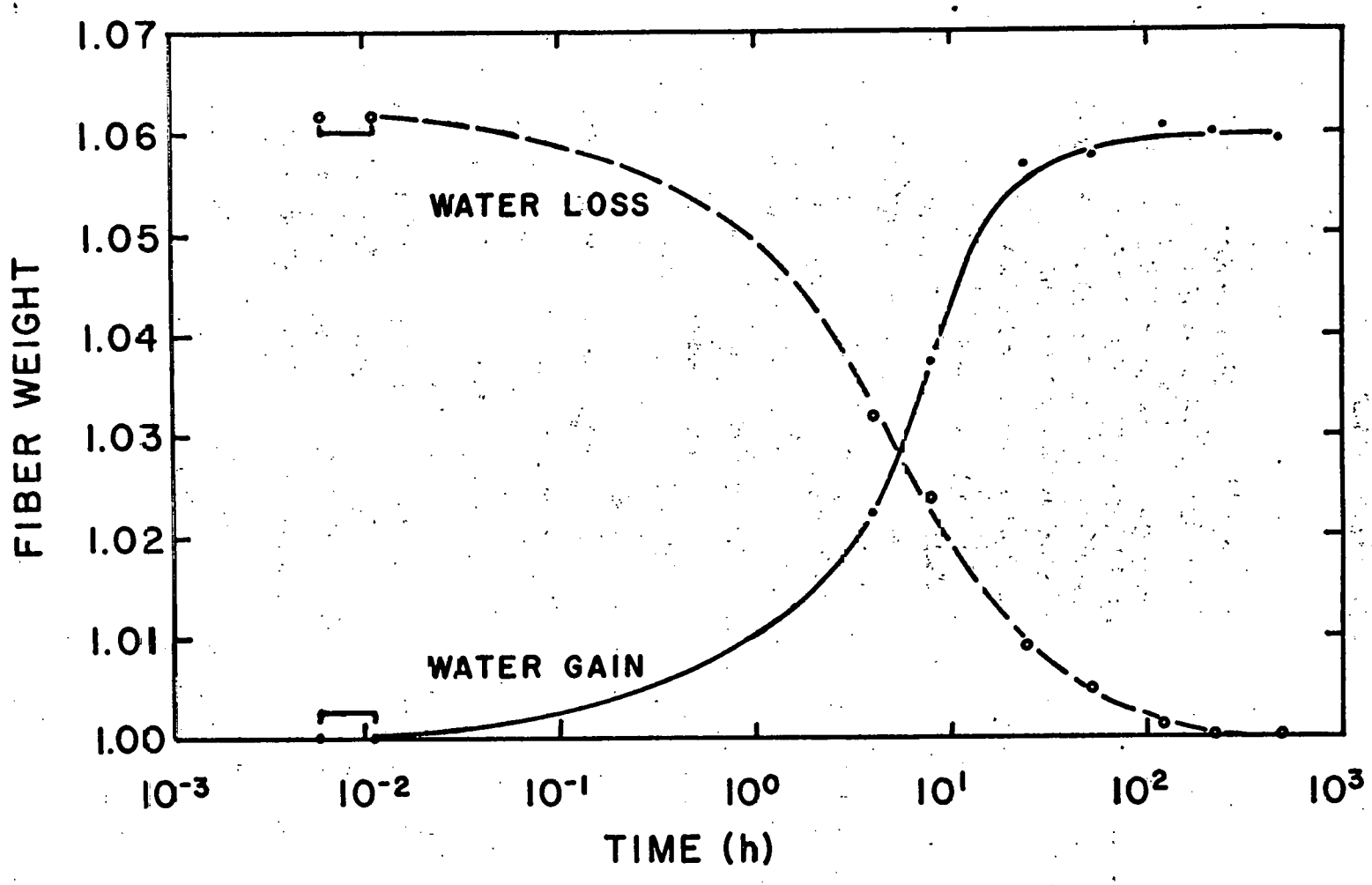

Figure 1. Water gain in 100%FH of Kevlar 49 from desiccated condition, and loss in 0%RH from saturated condition. The data spread at 10^{-2} h reflects the time it took to weigh the fiber. Weight is normalized to desiccated condition.

Composite Fabrication

Du Pont's Kevlar 49 roving, 195 denier, was used exclusively. The epoxy resin was DER 332 (Dow Chemical Co.) cured with Jeffamine T-403 (Jefferson Chemical Co.) prepared at 50°C in a weight ratio of 100 to 36, respectively.

After moisture equilibrium had been reached, fiber from each spool was circumferentially filament wound with epoxy into cylindrical sleeves approximately 10 cm long and 0.6 cm thick, onto a 9.5-cm diameter aluminum mandrel with a dodecagonal cross section (Fig. 2a). To insure that wet fiber would not lose appreciable water to the atmosphere, nor dry fiber gain water, each spool was quickly transferred from its jar to a plastic box, maintained at the same atmospheric condition, from which the winding was done. Transit time of the fiber from its box to the resin pot, and thence to the mandrel during winding, was of the order of several seconds, not long enough for a significant amount of water to be gained by the dry fiber from the atmosphere. However, the probable loss of water from wet fiber in the winding process by other than evaporation is discussed below.

Four fiber-epoxy cylinders were wound side by side, two each from wet and dry Kevlar 49. After 24 h, a wet-fiber and a dry-fiber cylinder were removed, representing the 20°C cured condition. The other two cylinders, still attached to the mandrel, were postcured for 16 h at 75°C. The dodecagonal cross section of the mandrel permitted the cutting of flat, composite specimens from each cylinder. The finished pieces, six from each cylinder, were rectangular bars, 5 cm long, 1.27 cm wide, and 0.42 cm thick, the fibers being parallel to the 1.27-cm dimension.

Testing

The size and shape of the composite bars were chosen for a three-point flexural test, with uniaxial strain gauges attached to the tensile faces. Cross-head speed speed was 0.05 cm/min. The formula for stress in the tensile face,[12]

$$\sigma = \frac{3PL}{2\,bd^2} \quad , \qquad (1)$$

was applied, where P is the load at failure, the other parameters being shown in Fig. 2b. The shortcomings of such a test in yielding a true tensile

strength were recognized, but difficulties were encountered with dogbone tensile samples; e.g., failure in the grips. Equation (1) applies strictly to materials for which the stress-strain relationship is linear to failure, and for which the strains are small, conditions not strictly met here (Fig. 3). However, the equation is valid for comparison purposes.[12]

Table I shows that the wet-fiber composites cured at 20°C were 16% weaker than the similarly cured dry-fiber composites; elastic modulus was correspondingly lower by 5%. The weakening effect was 20% for composites postcured at 75°C for 16 h; elastic modulus was 3% lower. The higher-temperature cure improved the flexural strength of dry-fiber composites by 30%, and the wet fiber by 23%; elastic modulus declined 4 and 2%, respectively.

Scanning electron microscopy of the fracture surfaces yielded little information, since the surfaces were poorly defined. No differences between samples were obvious, therefore.

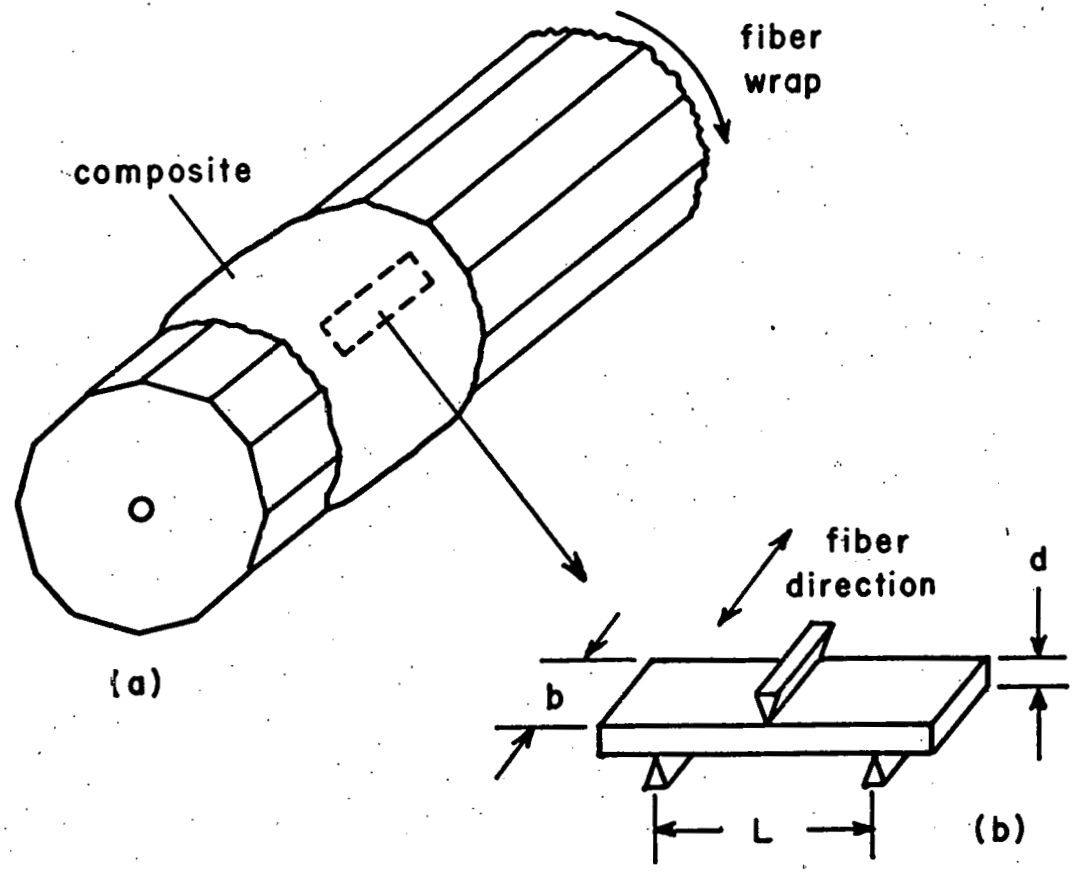

Figure 2. (a) Kevlar 49-epoxy circumferential wrap on 9.5-cm diameter dodecagonal mandrel. (b) Transverse flexural sample cut from composite, mounted on knife edges for testing.

Table I. Transverse flexural strength, failure strain, and elastic modulus of dry and wet 63.5 vol.% Kevlar-49-epoxy composites cured at 20 and 75°C

	Transverse Flexural Strength (MPa) Tensile Face			Transverse Flexural Failure Strain (%) Tensile Face			Transverse Flexural Elastic Modulus (GPa) Tensile Face		
	Outward	Inward		Outward	Inward		Outward	Inward	
Dry Kevlar 49-epoxy 20°C cure	32.8	28.7		0.578	0.514		6.00	5.94	
	30.6	28.3		0.540	0.520		5.90	6.00	
	31.2	30.0		0.560	0.521		5.76	6.32	
Average - each set	31.5	29.0		0.559	0.518		5.89	6.09	
Average - both sets			30.2			0.539			5.99
Wet Kevlar 49-epoxy 20°C cure	26.7	24.7		0.493	0.455		5.64	5.89	
	24.8	--		0.460	--		5.58	5.71	
	28.5	22.3		0.512	0.520		5.79	--	
Average - each set	26.7	23.5		0.488	0.488		5.67	5.80	
Average - both sets			25.4			0.488			5.72
Dry Kevlar 49-epoxy 75°C, 16 h cure	39.7	33.6		0.713	0.518		5.90	5.58	
	43.9	39.7		0.800	0.742		5.66	5.85	
	40.9	37.3		0.764	0.700		5.69	5.79	
Average - each set	41.5	36.9		0.759	0.587		5.75	5.74	
Average - both sets			39.2			0.723			5.75
Wet Kevlar 49-epoxy 75°C, 16 h cure	36.4	26.8		0.700	0.508		5.55	5.67	
	36.9	27.6		0.720	0.512		5.50	5.72	
	35.5	23.6		0.678	0.435		5.57	5.53	
Average - each set	36.3	26.0		0.699	0.485		5.54	5.64	
Average - both sets			31.2			0.592			5.59

All samples: Fiber volume fraction = 63.5 ± 1.9 vol.%.
Bulk density = 1.335 ± 0.015 g/cc.

DISCUSSION

It is difficult to estimate how much of the water on the surface of the fibers equilibrated to 100%RH actually became incorporated in the composite. The roving passed over several pulleys and through the resin pot before contacting the mandrel; a large, but undetermined, amount of water must have been lost in the process. However, any water that remained on the fiber would have interfered with the fiber-matrix bond. Glycols produced by the reaction between water and epoxy resin[3] would probably act as plasticizers or flexibilizers. A sufficient amount of these agents will reduce both strength and modulus,[13] and when localized at the fiber-resin interface, would mechanically decouple the fiber from the matrix. If water competes with the curing agent for the resin, then free curing agent will be present in the cured epoxy. Evidence for this was found in a DER 332/T-403 epoxy to which several percent water was added when the system was being prepared. A cure at 75°C for 16 h produced a yellowing of the epoxy which was taken as evidence of oxidation of the T-403 which, alone, yellows with age. The epoxy, without water added, does not discolor. Discoloration of the post-cured samples containing wet fiber could not be detected because of the naturally yellow color of the Kevlar 49. The slightly lower value of elastic modulus in the wet-fiber composites could be evidence of the formation of glycols and the presence of free curing agent.

In a composite with poorly bonded fibers, the matrix is likely to behave like a body weakened by cylindrical cavities. Other properties, not examined in this experiment, could also be affected. For example, shear strength should also decline.

The cure at 75°C for 16 h, improved the transverse strength of both wet- and dry-fiber samples by promoting more complete polymerization in resin not affected by water. (In this connection, the small decline of elastic modulus in the postcured composites is not understood.) The wet-fiber composites remain weaker than the dry. Other fiber-epoxy composites degraded in strength by water absorbed <u>after</u> curing have been shown to recover their properties when dried by heating at 120 to 175°C.[7,11] However, the chemistry of the water-unpolymerized resin system of this experiment may be different from the supposed hydrogen-bond disruption in the others. The testing of wet- and dry-fiber samples exposed to temperatures higher than 75°C would be desirable.

CONCLUSIONS

1. Kevlar 49 fiber can extract up to 6% of its weight in moisture from the atmosphere when exposed to 100%RH for 100 h.
2. Room-temperature cured composites made of water-bearing Kevlar 49 fiber and DER 332 epoxy with the aliphatic amine curing agent, Jeffamine T-403, have 16% lower transverse flexural strength than those in which the fiber has been desiccated. Composites postcured at 75°C exhibit a similar effect--a 20% strength reduction.
3. It is suggested that the reduction in strength is due to the degradation of the interfacial bonds resulting from the reaction of water with epoxy to produce unpolymerizable glycols with a consequent excess of curing agent. The reaction is irreversible, at least to 75°C for 16 h.
4. Kevlar 49 should be dried well before filament winding if maximum transverse strength is to be realized.

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