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Carderock Division
Naval Surface Warfare Center
Bethesda, MD 20084–5000

CARDEROCKDIV–SME–92/38 January 1993

Ship Materials Engineering Department
Research and Development Report

Effect of Water Immersion on Fiber/Matrix Adhesion

by
Thomas Juska

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ABBREVIATIONS

°C	Degrees Centigrade
KSI	Thousand Pounds Per Square Inch
MSI	Million Pounds Per Square Inch
OCF	Owens Corning Fiberglas
PEEK	Polyetheretherketone
PEKK	Polyetherketoneketone
PPS	Polyphenylene Sulfide
SBS	Short Beam Shear
SEM	Scanning Electron Microscopy

ABSTRACT

A study was made on the effect of water immersion on fiber/matrix adhesion in composites. Representatives of the four main classes of continuous fiber composites were tested: glass/thermoset, carbon/thermoset, glass/thermoplastic, and carbon/thermoplastic. Water conditioning was done by immersion in 50 °C distilled water. The only class of composites degraded by water was glass-reinforced thermoplastics. However, carbon-reinforced vinyl esters, a subset of the carbon/thermoset class, appear to have weak fiber/matrix bonds when dry, and these bonds are further degraded by water. In both cases, immersion in water hydrolyzed the interfacial bonds and caused large, irrecoverable property reductions.

ADMINISTRATIVE INFORMATION

This project was sponsored by the Office of the Chief of Naval Research, Office of Naval Technology, under the Ship and Submarine Materials Block, and Program Element Manager J.J. Kelly. It was administered by Ivan Caplan, Block Manager CDNSWC Code 0115, under Program Element 62234N, Task Area RS34S56, and DTRC Work Unit 1-2802-603.

INTRODUCTION

The effect of water immersion on fiber/matrix adhesion in composites has been investigated by measuring interface-dominated mechanical properties before and after immersion in 50 °C distilled water. These properties were 0° compression, 90° flexure, and short beam shear. SEM microscopy was performed on the transverse flex failures to determine if fiber/matrix adhesion was degraded by water.

Fabric-reinforced materials were also included in the program. The layup used was all warps parallel, and the materials were tested in the warp direction. Interfacial adhesion has a substantial effect on the properties and hydrolytic stability of fabric-reinforced composites.

The goal of this program was to determine if water weakens fiber/matrix bonds. The approach was to measure changes in properties and observe changes in adhesion. The test methodology also allowed a qualitative assessment of fiber/matrix adhesion in the as-fabricated (dry) condition, in spite of the fact that bond strengths were not measured.

MATERIALS EVALUATED

Adhesion retention was evaluated on representatives of all four major classes of continuous fiber composites. The materials tested are described in Table I.

TABLE I - THE MATERIALS EVALUATED

MATERIAL	SIZE	SUPPLIER	FABRICATION
Glass/Thermoset			
S2/3501-6	OCF449	Hercules	Autoclave
A130/Hetron FR991	Tricompatible	Hexcel/Ashland	Hand-Layup
Carbon/Thermoset			
AS4/3501-6	g	Hercules	Autoclave
AS4/Epon 9405	w	Seemann Composites	RTM
AS4/Derakane 8084	w	Seemann Composites	RTM
XAS/Derakane 8084	g	Seemann Composites	RTM
Glass/Thermoplastic			
E/PPS	Proprietary	Phillips Petroleum	Press
E/J-2	OCF473	DuPont	Press
S2/PEEK	OCF933A	ICI-Fiberite	Press
S2/PEKK	OCF933A	DuPont	Press
S2/Vectra	OCF933A	Hoechst-Celanese	Press
Carbon/Thermoplastic			
AS4/PPS	-	Phillips Petroleum	Press
AS4/J-2	-	DuPont	Press
AS4/PEEK	-	ICI-Fiberite	Press
AS4/PEKK	-	DuPont	Press

PROCEDURE

Unidirectional materials were studied, when available, because interfacial adhesion plays a larger role in their properties than in any other layup. Two properties which readily reveal the degree of fiber/matrix bonding are 0° compression [1] and 90° flexural strength [2], so emphasis was placed on these values. (Transverse tensile strength is not a good substitute for transverse flexure since the former is flaw-controlled [2].) The short beam shear test was included in the program as a supplement to unidirectional compression and transverse flexure, but the SBS test results are generally more difficult to interpret [3].

In addition to the three mechanical properties mentioned, the effect of water immersion on adhesion was studied by scanning electron microscopy (SEM) on the 90° flex failures. It was found in this study that microscopy was effective at assessing the quality of the interfacial bond only if performed on the transverse flexure (or transverse tension) failures. Microscopic inspection of compression and shear failures did not reveal the condition of the interface.

WATER CONDITIONING

The samples were conditioned by immersion in 50 °C distilled water. Specimens from each material were machined to the appropriate dimensions for the three tests, and were weighed on a Mettler Gram-atic balance to 0.0001 gram prior to immersion. The samples were weighed periodically to determine rate of water absorption, and to assure saturation.

RESULTS

The effect of water immersion on composite strength are presented as percent retention of the properties. The focus of this report is on changes in the material caused by water.

GLASS/THERMOSET

The two glass/thermosets tested had excellent retention of adhesion following immersion, as shown in Figure 1. The property reductions are thought to be due to matrix plasticization. Microscopy before and after immersion did not indicate a loss in adhesion.

The technology of glass roving sizes and glass fabric finishes is mature. There are effective coupling agents for most (if not all) thermosets used as composite matrix resins, so achieving adequate, hydrolytically stable bonds between resin and glass is not a problem in the industry. However, the appropriate size/finish must be specified. If a vinyl ester resin is used with glass sized or finished for epoxies, for example, the material will have low strength and poor hydrolytic stability.

CARBON/THERMOSET

A single representative of this class was evaluated as a unidirectional composite, AS4/3501-6, whose property changes are reported in Figure 2. The most surprising change caused by water was the large decrease in transverse flex strength. Judging by the retention of compression strength and the appearance of the failure surfaces, interfacial adhesion was not reduced. Desiccation resulted in full recovery of the 90° flex strength.

Carbon fabric reinforced vinyl esters were found to have poor adhesion. Evidence for this is given in Figure 3, where the properties of carbon/vinyl ester are compared with those of carbon/epoxy. Carbon/vinyl ester compatibility was evaluated with AS4w, XASg, and T300 UC309. Microscopy shows excellent adhesion in the carbon/epoxy material, and almost bare fibers in the vinyl ester. Carbon fiber sizes generally have compositions compatible with epoxies, but these coatings are not compatible with vinyl esters. All carbon fiber sizes have not yet been tested, so it is possible one or more exi hich effectively couple carbon to vinyl ester.

GLASS/THERMOPLASTIC

This class of advanced composites was the most degraded by water immersion. As-fabricated materials appeared well-bonded and had good properties, but water rapidly hydrolyzed the bonds and reduced the strength. As an example, the reduction in SBS strength of S2/PEEK as a function of days immersion is given in Figure 4, together with the weight gain. Microscopy clearly shows a substantial loss in fiber/matrix adhesion after exposure to water. Property retention data for the five materials evaluated is shown in Figure 5. E/PPS, S-2/PEEK, and S-2/Vectra lost the most strength, and microscopy indicates a substantial loss in fiber/matrix adhesion. S-2/PEKK appeared to retain both adhesion and mechanical properties, however, testing after 20 months immersion shows that debonding does occur in this material. Only E/J-2 showed no evidence of adhesion loss.

This behavior does not follow a clear trend. For example, J-2 is a hydrophilic polymer, absorbing about 5% water when saturated. Yet, water immersion does not degrade the fiber/matrix bond. (E/J-2 showed only a slight reduction in compression strength after one year continuous immersion. Plasticization caused by the water absorption is thought to be responsible for the decrease in SBS and 90° flexural properties; these properties show good recovery upon desiccation.) On the other hand, PEEK is hydrophobic, absorbing less than 0.5% water at saturation. And despite the chemical similarity between PEEK and PEKK, and that the same reinforcement (OCF S2 933A) was used in both cases, there appeared to be a large difference in capacity to retain adhesion after exposure to water.

Like E/PPS and S-2/PEEK, S-2/Vectra is a glass-reinforced thermoplastic which loses adhesion upon exposure to water. The large mechanical property reductions and bare fibers on the water-conditioned transverse flex failure both lead to the conclusion that water somehow weakens the fiber/matrix bonds. The matrix appears to be well-adhered to the fibers prior to immersion. As an aside from the theme of this paper, it is worth noting that the very high Young's modulus (greater than 1 msi) of Vectra did not translate into high composite compression strength [4], as was expected.

CARBON/THERMOPLASTIC

All four carbon/thermoplastics tested had excellent fiber/matrix adhesion, both dry and water-conditioned. The data appears in Figure 6. Slight matrix-dominated property reductions of AS4/J-2 can be attributed to matrix plasticization, because the properties returned upon desiccation.

The most peculiar behavior of the carbon/thermoplastic class is the consistent increase in uniaxial compression strength which results from exposure to water, especially in AS4/PEEK. It is not clear what the water does to affect the compression strength in this manner.

SUMMARY

1. The four main classes of continuous fiber composites, glass/thermoset, carbon/thermoset, glass/thermoplastic, and carbon/thermoplastic, were tested for retention of fiber/matrix adhesion after extended immersion in 50 °C distilled water.

2. Measurements of interfacial shear strength were not made. The degree of adhesion retention was indirectly assessed by testing unidirectional composites for interface-sensitive mechanical properties, namely, 0° compression, 90° flexure, and short beam shear. These tests were augmented by microscopic inspection of the 90° flex failures.

3. Glass/thermoset fiber/matrix adhesion is not degraded by water if the appropriate size or finish is used.

4. Of the carbon/thermosets evaluated, only vinyl esters had inadequate fiber/matrix adhesion, and as a result, had low strength with poor resistance to hydrolysis. The carbon/epoxy tested was well-bonded initially and did not sustain a reduction in fiber/matrix adhesion after exposure to water.

5. The carbon/thermoplastics tested remained well-bonded after water immersion.

6. Glass/thermoplastics were the most degraded by water. E/PPS, S-2/PEEK, and S-2/Vectra all sustained permanent reduction in fiber/matrix adhesion after immersion in water, resulting in a large drop in mechanical properties. Adhesion loss in S-2/PEKK occurred more slowly. It can probably be stated that bonds were hydrolyzed, that is, water breaks some of the bonds between polymer and fiber size. Of the glass/thermoplastics tested, only E/J-2 showed adequate retention of fiber/matrix adhesion after water immersion.

REFERENCES

1. C. Megerdigian, R. Robinson, and S. Lehmann, "Carbon Fiber/Matrix Interphase: Effect of Carbon Fiber Surface Treatment and Environmental Conditioning on Composite Performance", Proceedings of the 33rd International SAMPE Symposium, March 7-10, 1988, page 571-582.

2. D.F. Adams, T.R. King, and D.M. Blackketter, "Evaluation of Transverse Flexure Test Method for Composite Materials", Composite Science and Technology, Vol 39, 1990, page 341-353.

3. J.M. Whitney and C.E. Browning, "On Short-Beam Shear Tests for Composite Materials:, Experimental Mechanics, Vol. 25, No.3, page 294-300, September 1985.

4. R.J. Palmer, "Investigation of the Effect of Resin Material on Impact Damage to Graphite/Epoxy Composites", NASA Contractor Report 165677, March 1981, page 53.

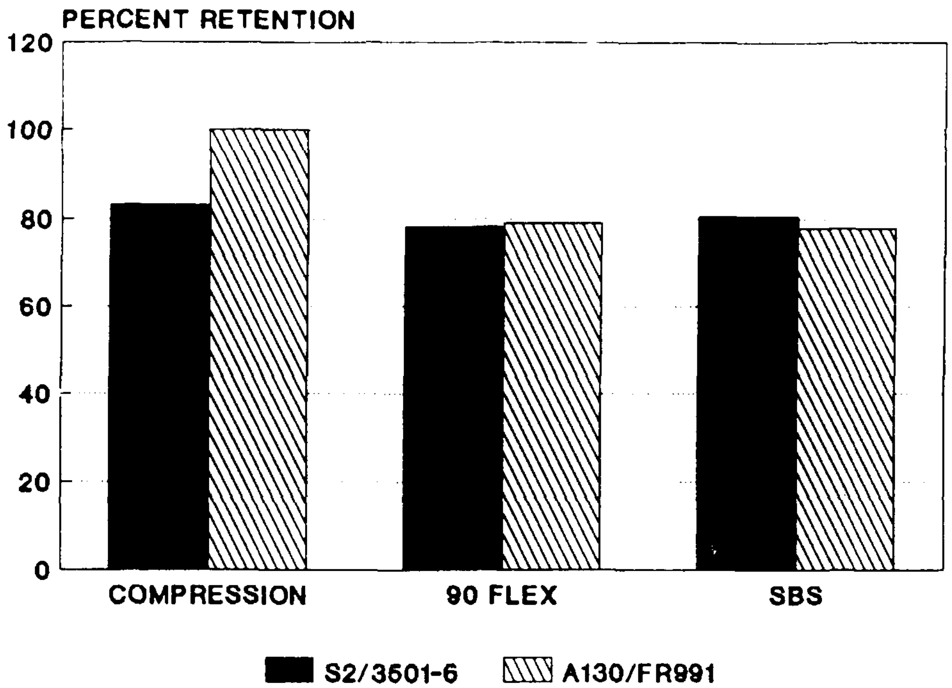


Figure 1. Effect of 9 month water immersion on the strength retention of glass/thermoset composites.

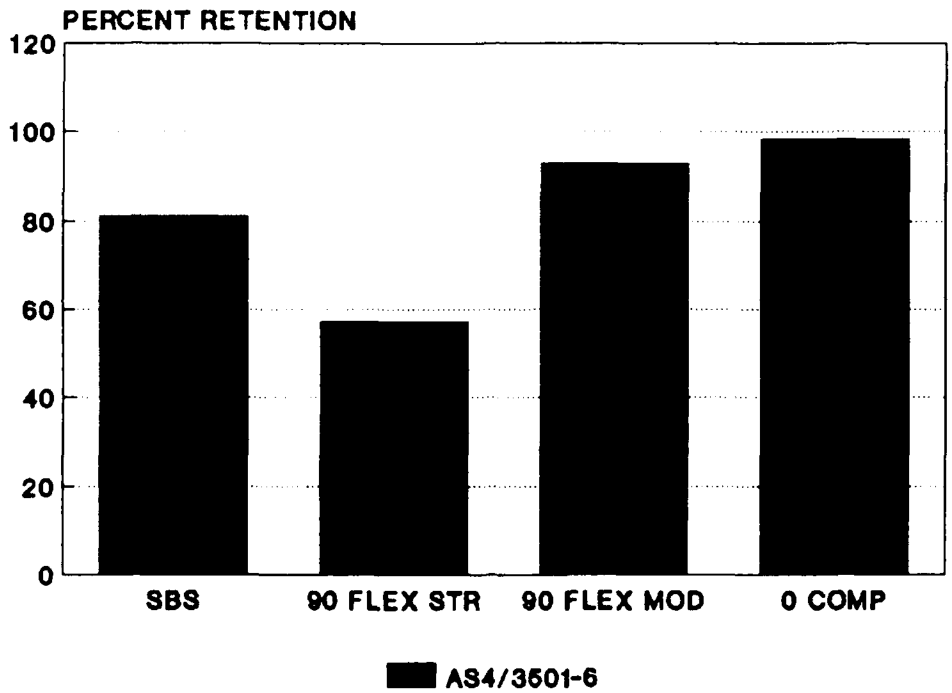


Figure 2. Effect of 9 month water immersion on the strength retention of carbon/thermoset composites.

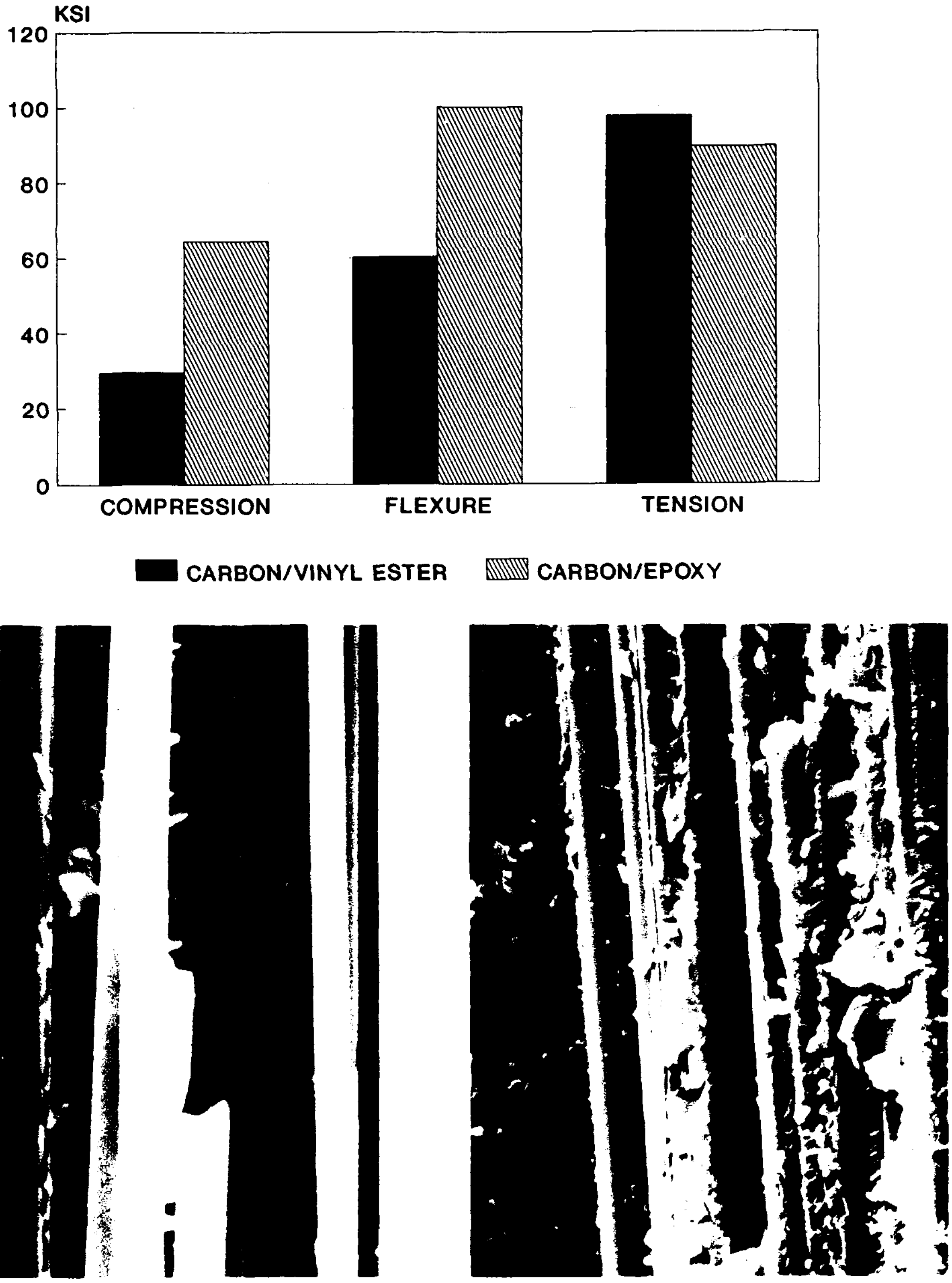
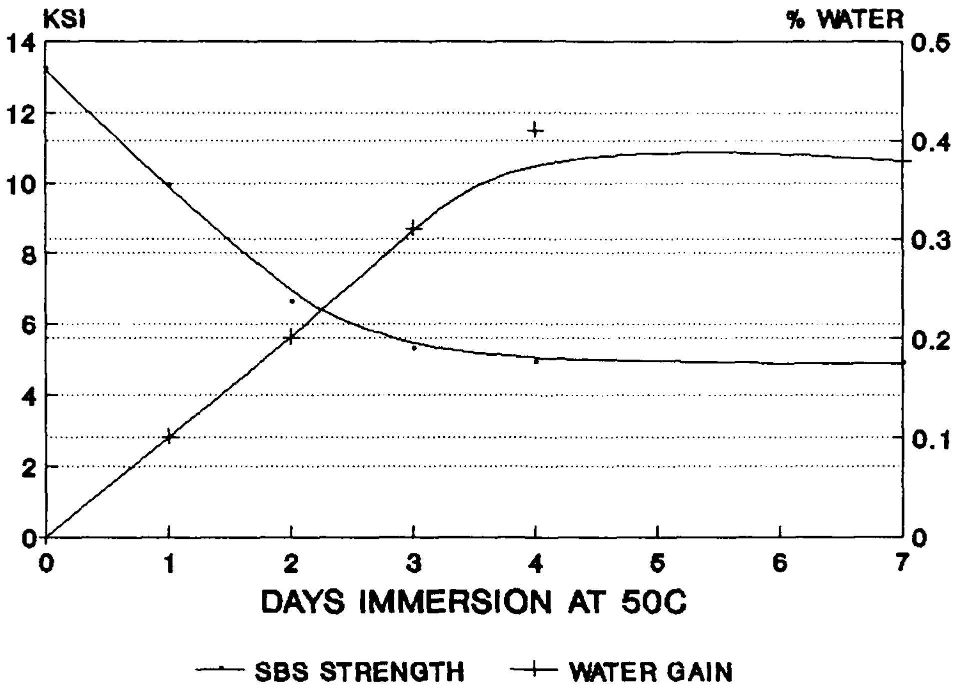


Figure 3. Evidence for poor interfacial adhesion in carbon/vinyl ester (left photo), showing low strength and bare fibers. The carbon/epoxy appears well-bonded (right photo) and has good properties.



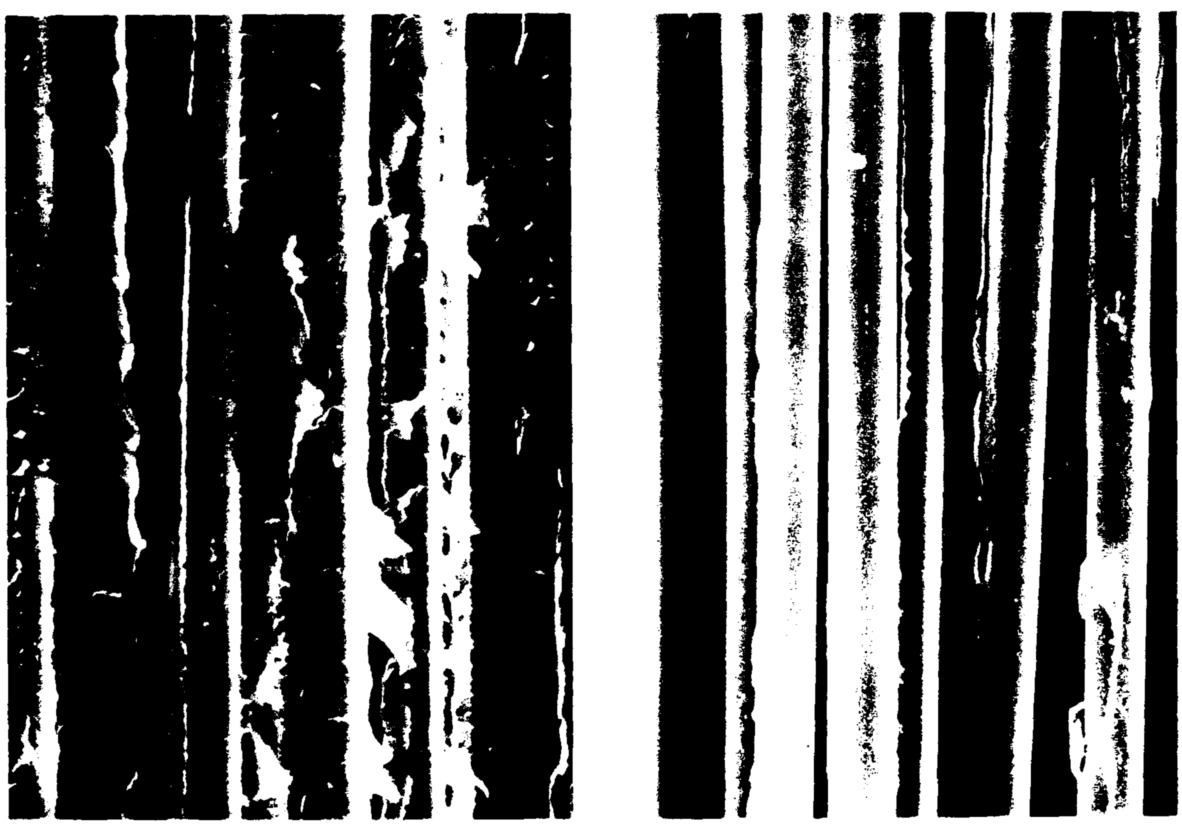


Figure 4. SBS strength of S2/PEEK vs. days immersion. The dry material (on left) appears well-bonded, but after 1 month immersion the adhesion is lost.

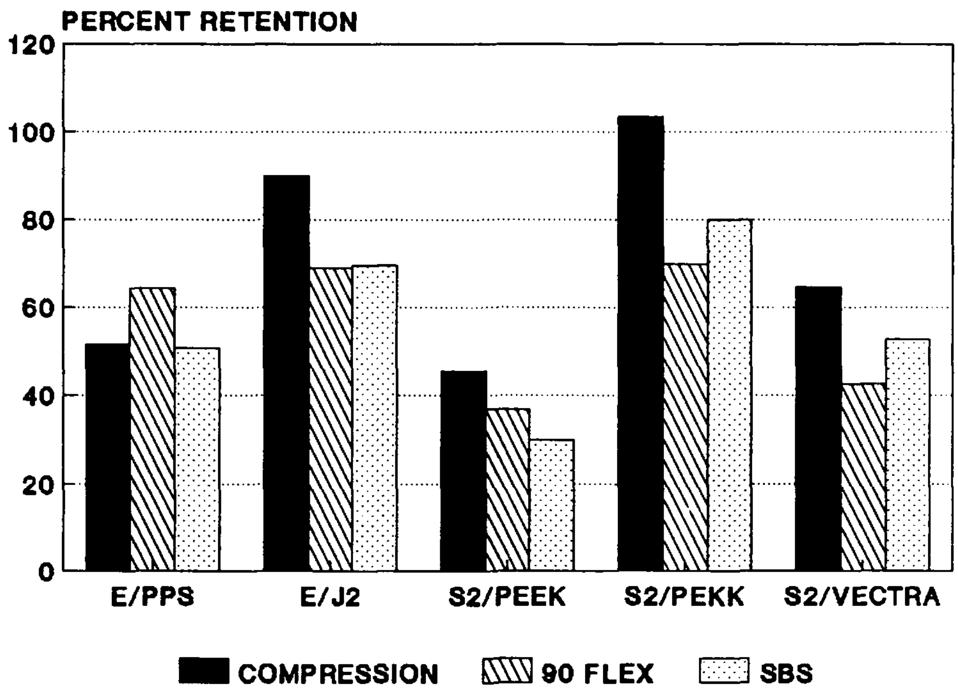


Figure 5. Effect of 9 month water immersion on the strength retention of glass/thermoplastic composites.

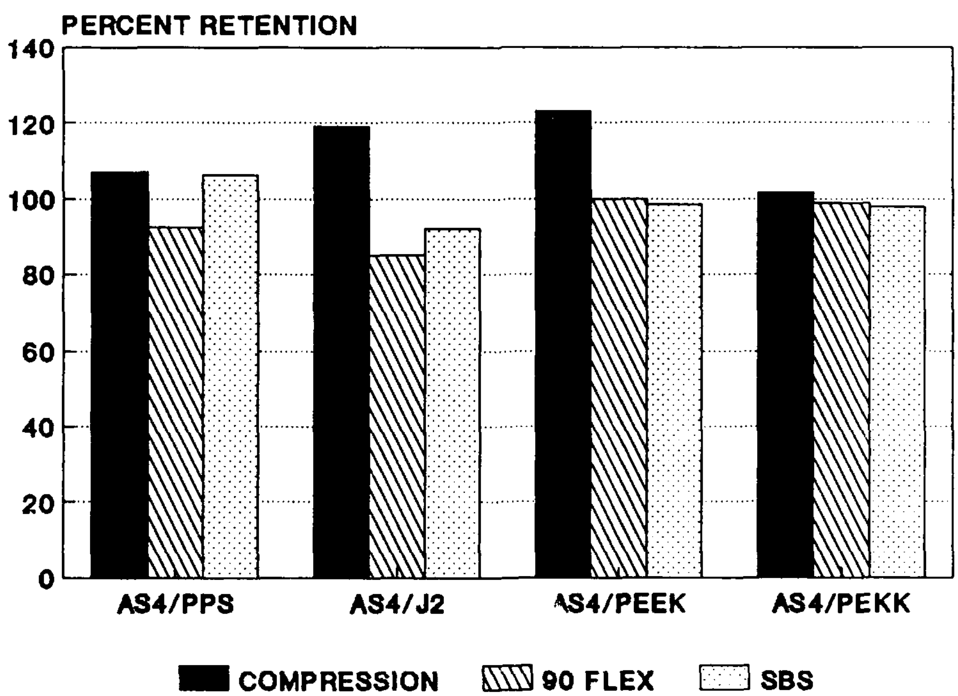


Figure 6. Effect of 9 month water immersion on the strength retention of carbon/thermoplastic composites.

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