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Interfacial adhesion of fiberglass reinforced thermoplastic composites

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INTERFACIAL ADHESION OF FIBERGLASS
REINFORCED THERMOPLASTIC COMPOSITES

David Gascoyne

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of the requirements for
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ABSTRACT

The use of reinforced plastics is vast. A proper understanding of these materials and their properties is important. The interface of a reinforced plastic influences many of the materials mechanical properties.

This study of fiber reinforced composites was conducted to better understand the interfacial interactions between XENOY and E-Glass fibers. The research consisted of studying the effects of processing temperature, long term hydrolytic attack, and coupling agents, on the interface.

ACKNOWLEDGMENTS

TABLE OF CONTENTS

TABLE OF FIGURES

INTRODUCTION:

Properties of fiber-resin composites are affected by a number of factors, including the "strength and modulus of the fiber, strength and chemical stability of the matrix, and the effectiveness of the bond between matrix and fiber in transferring stress across the interface."[1] The combination of fiber, resin and interface influences composite properties such as toughness, resistance to the environment, strength, and stiffness.

The interface is the region between the fiber and matrix where bonding between these two components occurs. Fiberglass is treated in two ways. One method, called sizing includes treating the glass with a lubricant, binder, and coupling agent. The lubricant prevents abrasive damage to the delicate glass fibers. The binder is used to improve packing of the glass fibers into strands, mainly by reducing static electricity. The coupling agent improves the bond between the glass and thermoplastic matrix.

The second type of glass treatment is called a finish. Glass fibers that are treated with a finish are initially treated with a size during production. The fibers are then

usually formed into a fabric or plied. The size prevents fiber
damage during this process. The size is next removed by
heating and the finish is applied. A finish is a coupling
agent which also acts as a lubricant.[4]

To maximize mechanical properties it is important to
transfer stress in all parts of the composite under a wide
variety of environmental conditions, over a long period of
time. Stress transfer between the glass fiber and
thermoplastic matrix occurs at the interface of the two
components. The main purpose of the coupling agent is to
bridge the organic-inorganic gap at the interface so stress
transfer can occur throughout the composite.[4]

Coupling agents generally come from a group of
chemicals called organo-silanes. Silanes are applied to the
glass surface to improve adhesion. One widely accepted theory
of adhesion promotion by silanes is the chemical bond theory.
Silane finishes, or coupling agents, have silicon atoms which
may form -Si-O-Si- covalent bonds to the glass.   The
coupling agent also has functional groups which may react with
functional groups on the polymer. It has been suggested that
the silane may work as a "bridge" over the organic-inorganic
interface. Adhesion may be improved by the silane through
interpenatration of the silane chains with the polymer matrix.
Coupling agents may increase the surface wettability of the
fiber. This would allow the matrix to wet out the glass

better. Better wetting will decrease voids at the interface.
Improved adhesion at the interface is not always desired.
Poorer adhesion may give a tougher composite and may therefore
be desirable. At the same time poor adhesion will decrease
composite strength. Many different coupling agents are
available. They may improve adhesion by all or some of the
mechanisms above.

EXPERIMENTAL:

The interfacial shear strength between glass fibers and
polymers was measured using a specially designed apparatus.
This instrument was designed at General Electric Corporate
Research and Development to produce a simple, quick, and
reliable test for measuring interface strength. The apparatus,
shown in Figure 1 consists of a load cell, load frame,
motorized actuator, one axis translational stage, and a
microcomputer for data storage. Samples are hung below the
balance by a wire connected to it. Two metal blades shown in
Figure 2 attached to the stage are positioned so that they
nearly touch the fiber on the sample. The stage is lowered by
reversing the motor. The lowering stage drives the blades down
the fiber and onto the bead. The force is measured twice every
second and transferred to the computer.   The force needed to
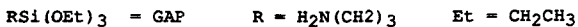debond the thermoplastic bead is between 10-90 grams, depending

on the interfacial contact area and strength of the bond. Data is transferred to a floppy disc for storage after each test.

Samples consist of a single glass fiber with an average diameter of 22 microns. An axisymmetric polymer bead is formed on the fiber as in Figure 2. The polymer beads are formed in the following manner. Sheets of brass are cut into tabs 1 x 2 cm. First, the ends of the glass fiber are taped to the tabs. The tabs and fiber were then mounted on a sample holder between two alligator clips. XENOY pellets were then heated at 300 °C for five minutes in a nitrogen atmosphere in a convection oven to create a melt of the polymer. The nitrogen atmosphere inhibits degradation of the polymer. Polymer threads were drawn from a crucible of this melt with forceps. The polymer threads had a diameter of 10 to 50 microns. The threads were then tied in knots around the glass fiber and the ends of the polymer clipped close to the knot. The knot was then partially melted to the glass with a soldering iron. This prevents the knot from slipping on the fiber in the convection oven. The sample was then placed in the oven at 270 °C in a nitrogen atmosphere for ten minutes. When removed from the convection oven the polymer formed an axisymmetric bead on the fiber. The length of the bead was measured using an optical microscope. The sample was hung from the test instrument and the force required to "debond" the thermoplastic from the glass fiber was measured.
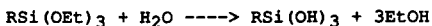
The system studied was E-glass/XENOY. XENOY is General Electric's trade name for a blend of polycarbonate (PC) and polybutylene terephthalate (PBT). XENOY combines the toughness of PC with the solvent resistance of semi-crystalline PBT to produce desirable mechanical properties with environmental resistance. A typical processing temperature for XENOY is 230 to 270 °C.

The starting fibers were E-glass coated with a 0.2 to 0.3 weight percent cationic lubricant. Fibers were obtained from Pittsburg Plate Glass Industries (PPG). The composition of the lubricant is proprietary to PPG and therfore unknown. The glass was not heat treated to remove the lubricant because heat treating degrades the glass properties.

A coupling agent was applied to the glass fibers. The coupling agent was γ-Aminopropyltriethoxysilane (GAP). To coat the glass with GAP the desired weight percent solution was prepared in water. This solution was stirred at room temperature for one hour. The glass was soaked in the silane solution for one minute, removed, and heated at 110 °C for thirty minutes. "Deposition from aqueous solution is employed for [applying silanes to] most commercial fiberglass systems."[3] Basic reactions of the silane with the glass are outlined below.

$RSi(OEt)_3$ = GAP   R = $H_2N(CH2)_3$ Et = CH_2CH_3

1. <u>Hydrolysis:</u>

$$RSi(OEt)_3 + H_2O \longrightarrow RSi(OH)_3 + 3EtOH$$

2. <u>Condensation:</u>

```
                                    R    R    R
                                    |    |    |
        3RSi(OH)3 ----> 2H2O + HO-Si-O-Si-O-Si-OH
                                    |    |    |
                                    OH   OH   OH
```

3. <u>Reaction with glass:</u>

```
    R    R    R                                R    R    R
    |    |    |                                |    |    |
 HO-Si-O-Si-O-Si-OH                         HO-Si--O-Si--O-Si--OH
    |    |    |           (hydrogen             |    |    |
    OH   OH   OH          bonding)              O    OH   OH
                          ---------->          / \
    +                                         H   H
    OH   OH   OH                               \ /
 ___|____|____|____                            O    OH   OH
                                            ___|____|____|___
    E-glass surface                           E-glass surface
```
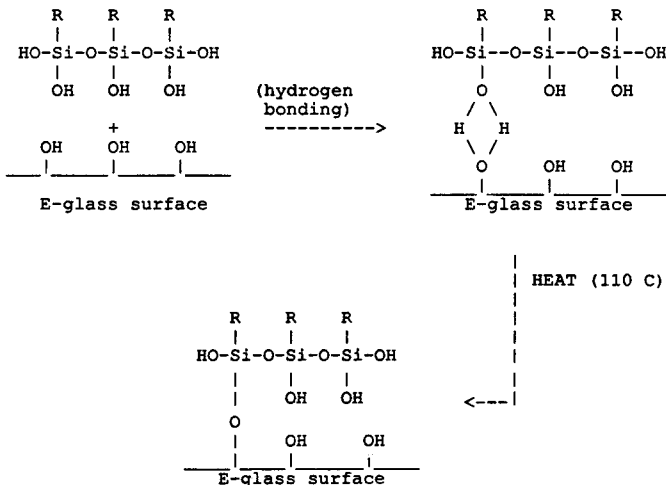
```
                                                    |
                                                    | HEAT (110 C)
                                                    |
        R    R    R                                 |
        |    |    |                                 |
     HO-Si-O-Si-O-Si-OH                             |
        |    |    |                                 |
        |    OH   OH                                |
        |                                  <---|
        O    OH   OH
        |    |    |
     ___|____|____|___
        E-glass surface
```
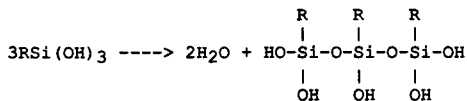
Steps one and two occur when the silane solution is prepared in the distilled water solution. The solution is allowed to stir at room temperature for one hour before the glass is treated. In step three the organosilane is adsorbed on the glass surface. Rapid adsorption of GAP accurs in the first thirty seconds and the coating continues to slowly build up during the last thirty seconds.[4] Heating the glass begins the bond formation between hydroxyl groups on the glass and GAP. The organosilane usually will only form one bond from each silicon to the E-glass surface. The other two silanol groups either bond to other coupling agent silicon atoms or are in free form.

RESULTS:

A plot of force vs. time is shown in Figure 3. The force increases linearly until debonding occurs. After debonding the mass drops to zero and then levels out at a mass of a few grams. When debonding occurs the elastic energy stored in the fiber is released. This energy drives the bead down ahead of the blades resulting in a force reading of zero until the blades catch up to the bead. Once the blades catch up to the bead dynamic friction at the interface gives a small force reading on the balance.

Strength is a statistical measurement. As with all statistical measurements there is a certain amount of uncertainty. To help average out uncertainty in a given study, 15 to 20 beads of different lengths were debonded. The interfacial shear strength (τ) is related to the force (F) and contact area (A) by the equation

$$\tau = F\ A.[7]$$

(1) A graph of force to debond versus interfacial contact area has a slope equal to the interfacial shear strength. The plot is linear and extrapolates through the origin as Equation 1 predicts.

The load/time printout for a single test is shown in Figure 4. The contact length (1) is related to contact area (A) by the equation

$$A = \pi d l.[7]$$

(2)   An average diameter (d) of 22 microns was used for the glass fibers.   The force readings were converted into force values in newtons.   A graph of force versus area has a slope equal to the interfacial shear strength.

To determine the interfacial shear strength between the polymer and glass, 15-20 samples were prepared and tested.   The contact length of the samples range from 100 to 300 microns. The debond force versus bead length was plotted for each sample. An example is shown in Figure 5.   These plots ideally are linear and extrapolate through the origin as suggested by Equation 1.

DISCUSSION:

Three adhesion studies were performed. The effects of coupling agent coating thickness, processing temperature, and hydrolytic attack on the interfacial bond were examined.

Interfacial shear strength was measured between XENOY and PPG's E-glass fibers coated with GAP from different weight percent solutions. Shear measurements were made on dry samples and on samples that were soaked in water for one hour at 40 °C. The results are presented in Table 1 and Figure 6.

TABLE 1
Interfacial Shear Strength After Normal Processing
and After Soaking 1 Hour in Water at 40 C.

Fiber coating (MPa)	τ (dry) (MPa)	τ (1 hour in water)
.2-.3% cationic lubricant	33 ± 3	19 ± 3
from 0.5% GAP solution	37 ± 3	37 ± 4
from 1.0% GAP solution	41 ± 4	36 ± 4
from 5.0% GAP solution	44 ± 4	36 ± 4
from 30 % GAP solution	42 ± 4	37 ± 4

Thermogravimetric Analysis (TGA) was used to determine
the loading of GAP on the glass. TGA monitors the weight of a
sample throughout a temperature cycle. After glass is heated
to 700 °C all the coatings should be burned off. Samples of
silane treated glass and lubricated glass are weighed before
and after TGA. The weight percent of silane and lubrication
coatings were then determined. TGA results for the glass in
Table 2 and Figure 7 show that the weight percent of GAP
deposited on the glass increases with solution concentration.
The change in dry interfacial shear strength with silane
loading is shown in Table 1 and Figure 6. Dry adhesion is
sensibly independent of fiber loading. The lubricated fibers
form an effective bond to the matrix in the absence of water.
The silane treated fibers produce dry adhesion that is 11-25%
better than the lubricated fibers. The importance of the GAP
coating becomes apparent when samples are soaked in water for
one hour at 40 °C. The adhesion between lubricated fibers and
XENOY decreases by 42% after one hour in the water. GAP coated
fibers have a minimal loss in adhesive strength after this same
time.

TABLE 2

Results from Thermogravimetric Analysis of E-glass fibers

Fiber coating	weight percent of coating removed during TGA (Average of three trials)
0.2-0.3 % cationic lubricant	.29 %
From 0.5 % GAP solution	.44 %
From 1.0 % GAP solution	.49 %
From 5.0 % GAP solution	.91 %
From 30 % GAP solution	4.5 %

Adhesion between lubricated fibers and XENOY decreases
when samples are soaked in water for a short time. It is known
that water forms strong hydrogen bonds with hydroxyls on the
glass surface. Water will compete with any possible bonds
between polymer and the glass surface. The chemical bonding
theory provides an explanation for improved adhesion with
silane coupling agents. "Silanols in contact with a water
covered hydrophilic surface are uniquely capable of competing
with water because of their capacity for strong hydrogen
bonding. Although any individual bond of coupling agent with a
[glass surface] is hydrolyzable the reversible nature of their

hydrolysis prevents complete loss of adhesion."[1]   There is
some loss of strength even when GAP coated samples are soaked
in water, however, the loss is not as great as the lubricated
glass samples.

The long term hydrolytic stability of the interface was
also examined. Samples consisting of Xenoy beads on GAP coated
and lubricated fibers were soaked in water at 40 °C for times
from 1 to 120 hours. Shear strength values are shown in Table
3 and Figure 8. Adhesion between lubricated fibers and XENOY
drops off dramatically after one hour in water. The
interfacial bond strength plateaus after about 40 hours in
water at 14 MPa. Fibers treated with a silane solution retain
their interfacial strength for several hours. Gradual loss of
adhesive strength is seen with the silane treated fibers.
Interfacial strength plateaus at 35 MPa after 40 hours with the
silane treated fibers.

Water at the interface will set up strong hydrogen bonds
with hydroxyl groups on the glass surface. Several layers of
water may build up at the interface. Water at the interface of
samples prepared with lubricated fibers will destroy any
polymer/glass interactions, however, this would predict that
shear strength should fall off to zero. The plateau at 13 MPa
may be from the clamping of the XENOY bead to the fiber. XENOY
and glass have different coefficients of thermal expansion.
During sample preparation XENOY beads are formed on the glass

at 270 °C. When the samples cool XENOY will shrink more than the glass. The shrinking will clamp the bead to the fiber.

One possible explanation for the difference in plateaus comes from E. P. Pleuddmann's discussion of a silanes ability to compete with water for chemical bonds at the glass surface.[4] The silanol coating on GAP treated fibers will compete with water for available hydroxyl groups on the glass surface. The small loss of adhesion may be explained by an equilibrium between the water and silane for glass surface hydroxyls. Once equilibrium is established the shear strength plateaued at 35 MPa.

TABLE 3

Interfacial Shear Strength After Soaking in Water at 40 C.

FIBER COATING	Hours in Water Bath at 40 °C						
fiber coating	0	1	5	20	40	60	120
from 1.0 % GAP	41 ±4	39 ±4	41 ±4	38 ±3	35 ±5	35 ±4	31 ±3
.2-.3% cationic lubricant	33 ±3	19 ±3	19 ±3	15 ±5	14 ±3	13 ±2	13 ±2

To study the reversibility of damage to the interface caused by water, samples were prepared and soaked in water for

60 hours. These samples were then removed from the water and placed in a vacuum oven for 20 hours at 40 °C. The vacuum oven treatment was designed to remove any water from the samples. Results in Table 4 and Figure 8 show that the loss of interfacial strength is not reversible.

TABLE 4

Effect of Vacuum Treatment on Samples Soaked in Water

Fiber coating 20 (MPa)	τ after 60 Hrs. in water at 40 °C and then Hrs.in vacuum oven at 40 °C
from 1.0% GAP solution	35 ± 3
.2-.3 % cationic lubricant	15 ± 2

Processing temperature can also effect the interfacial bond strength. Samples prepared with silane treated glass and lubricated glass were processed at temperatures ranging from 230 to 330 °C. Results are shown in Table 5 and Figure 9. A normal processing temperature for XENOY is between 230 and 270 °C. When shear measurements were made with XENOY on silane treated glass and untreated glass the interfacial shear

strength was found to increase with processing temperature and
eventually level off. As processing temperatures get higher
the viscosity of the polymer decreases. The decrease in
viscosity allows the polymer to wet the fiber more thoroughly.
Better wetting will increase interactions between matrix and
fiber. The results from the lubricated fibers show that better
wetting will help to increase adhesion.

TABLE 5

Interfacial Shear Strength (MPa)
at Different Processing Temperatures ^{o}C.

			Temperature			
Fiber coating	230	250	270	290	310	330
from 1% GAP solution	36 ±4	36 ±4	41 ±4	43 ±3	44 ±4	43 ±5
.2-.3% cationic lubricant	27 ±2	31 ±2	36 ±3	40 ±3	43 ±4	43 ±3

Until a processing temperature of 310 ^{o}C is reached
adhesion between polymer and uncoated glass is lower than with
silane coated glass.

When very high temperatures are reached (i.e. 310 ^{o}C or
higher) the adhesion between polymer and silane treated glass

levels off. It is possible that the loss of adhesion at high
temperatures is due to polymer degradation. H. Ishida and K.
Nakata[2] showed that the degradation of PBT is catalysed by GAP.
To explain this leveling off at high temperatures the molecular
weight of Xenoy was measured in three different dry blends of
the polymer. The first blend consisted of a finely powered
Xenoy. The second and third blends contained the powered Xenoy
and a high surface area fumed silica. When heated the powered
XENOY ideally formed a thin layer on the high surface area
fumed silica. The thin layer of XENOY will simulate the
polymer/glass interface of an interfacial shear strength
sample. The fumed silica in the third blend was treated with a
1 % GAP solution. Gel Permiation Chromatography (GPC) results
show that in the third blend the number average molecular
weight, M(n), drops of drastically between 290 C to 310 °C.
When M(n) drops below 10,000 the polymer mechanical properties
may be effected. At very high temperatures there are two
factors effecting adhesion that are working against each other.
Better wetting should help to increase adhesion but the polymer
degradation is decreasing the strength of the polymer. These
two factors can explain the leveling of of silane treated
fibers in Graph 2. M(n) data in Table 5 and Graph 4 from the
first and second blend do not show any significant loss in
molecular weight. This evidence supports the shear strength
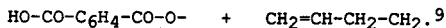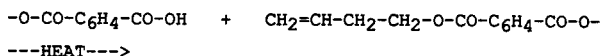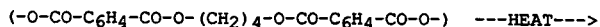data for pristine glass in Graph 2. Since there is no

degradation of Xenoy the interfacial shear strength of Xenoy on uncoated fibers continues to increase at high temperatures.

TABLE 6

Effects of Temperature on the Number Average
Molecular Weight [M(n)] of XENOY *

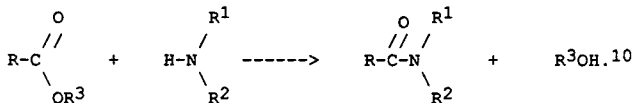| Sample	230	250	270	290	310	330
Xenoy	39,000	40,000	39,000	35,000	28,000	--
Xenoy and Fumed Silica	40,000	39,000	33,000	27,000	22,000	--
Xenoy & GAP coated Fumed Silica	--	36,000	27,000	30,000	9,800	--

* an average of M(n) of PC and PBT was recorded.

PBT is known to degrade at elevated temperatures by the following reaction

$(-O-CO-C_6H_4-CO-O-(CH_2)_4-O-CO-C_6H_4-CO-O-)$ ---HEAT--->

$-O-CO-C_6H_4-CO-OH$ + $CH_2=CH-CH_2-CH_2-O-CO-C_6H_4-CO-O-$
---HEAT--->

$HO-CO-C_6H_4-CO-O-$ + $CH_2=CH-CH_2-CH_2$.[9]

Ishida and Nakata[9] showed that this thermal degradation was catalyzed by the amine group of GAP. However, it is believed that the catalyzation reaction will only occur at the interface between GAP and PBT, not in the bulk PBT.

Another known reaction is that of esters with amines to form an alcohol and a ketone. The reaction is

$$
R-C\underset{OR^3}{\overset{O}{\big\backslash\!\!\!\big/\!\!\!\big/}} \quad + \quad H-N\underset{R^2}{\overset{R^1}{\big\backslash\!\!\!\big/}} \quad \longrightarrow \quad R-C-N\underset{R^2}{\overset{O\;\;R^1}{\big/\!\!\!\big/\;\big/}} \quad + \quad R^3OH.[10]
$$

This type of reaction could be responsible for degradation of both PBT and PC.

SUMMARY:

A novel fiber pullout test was used to study the adhesion between Xenoy and fiberglass. The interfacial shear strength between beads of polymer and the glass was measured. The adhesion was studied as a function of fiber loading, processing temperature, and exposure to water. Glass was coated with GAP from solutions with concentrations from 0.5 to 30 weight percent. Fiber loading increased with solution concentration. Adhesion was independant of solution concentration. Adhesion increases with processing temperature and comes to a plateau. The increase with temperature is probably due to better wetting of the fiber. The plateau may be due to degradation of the polymer. Untreated fibers lose interfacial strength after minimal exposure to water. GAP treated glass had some loss in strength after several hours of exposure but maintains a higher level of adhesion.

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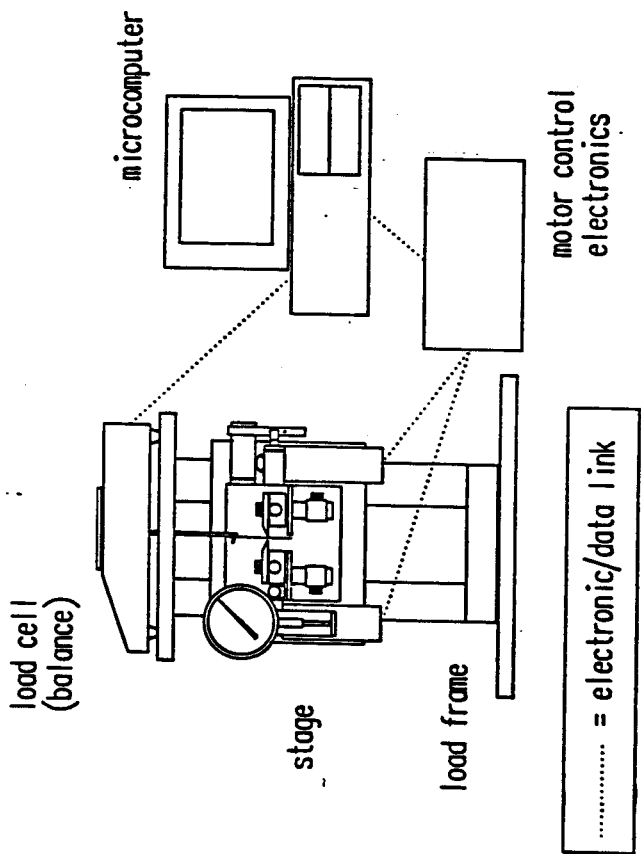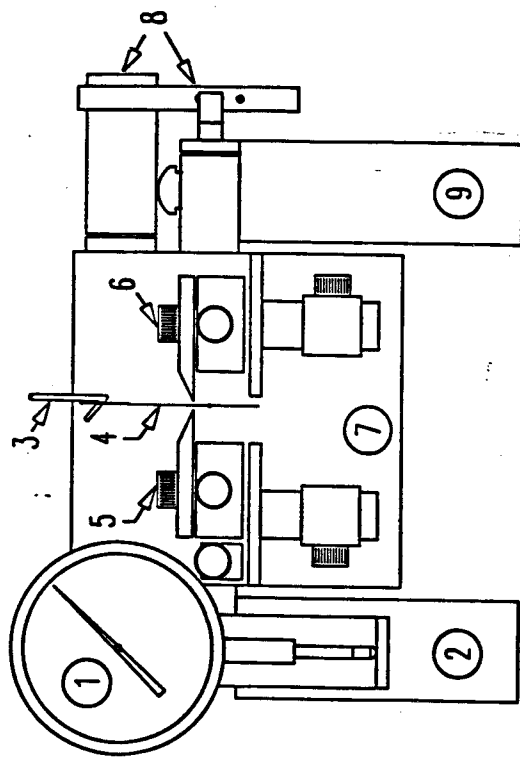
microcomputer

motor control
electronics

load cell
(balance)

stage

load frame

········· = electronic/data link

Figure 1

Figure 2

1. dial indicator
2. fast drive motor
3. hook from load cell
4. sample
5. translable blade
6. fixed blade
7. translation stage
8. optoelectronic limit sensor
9. slow drive motor

Microdebonding Test   09-11-1987   08:25:07

Sample: WC2-105
Resin: XENOY
Fiber: C2
Comment: 1.15
Motor Velocity: 1
Post test comment: 60 HRS. 40 C

1	+0.00	2	+0.00	3	+0.00	4	+0.00	5	+0.00
6	+0.00	7	+0.00	8	+0.10	9	+0.60	10	+1.40
11	+2.40	12	+3.55	13	+4.85	14	+6.25	15	+7.75
16	+9.35	17	+11.10	18	+12.80	19	+14.80	20	+16.5
21	+18.55	22	+20.55	23	+22.60	24	+24.60	25	+26.75
26	+28.75	27	+30.75	28	+30.25	29	+1.15	30	+0.00
31	+0.00	32	+0.00	33	+0.00	34	+0.00	35	+0.00
36	+0.05	37	+0.60	38	+1.45	39	+2.45	40	+0.00
41	+4.25	42	+4.50	43	+4.65	44	+4.70	45	+4.70
46	+4.60	47	+4.55	48	+4.55	49	+4.50	50	+4.45
51	+4.45	52	+4.45	53	+4.40	54	+4.40	55	+4.35
56	+4.30	57	+4.25	58	+4.20	59	+4.05	60	+4.05

Mass Applied to Thermoplastic Bead vs. Time

Mass (g)

Time

Figure 4

Debond Mass vs. Bead Length
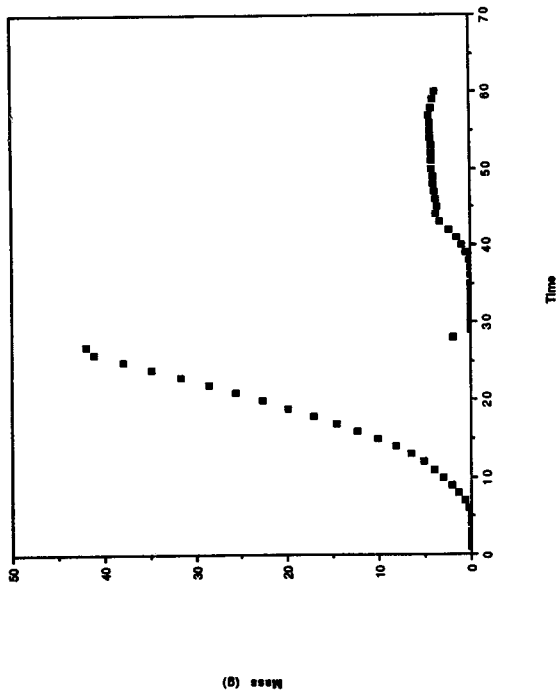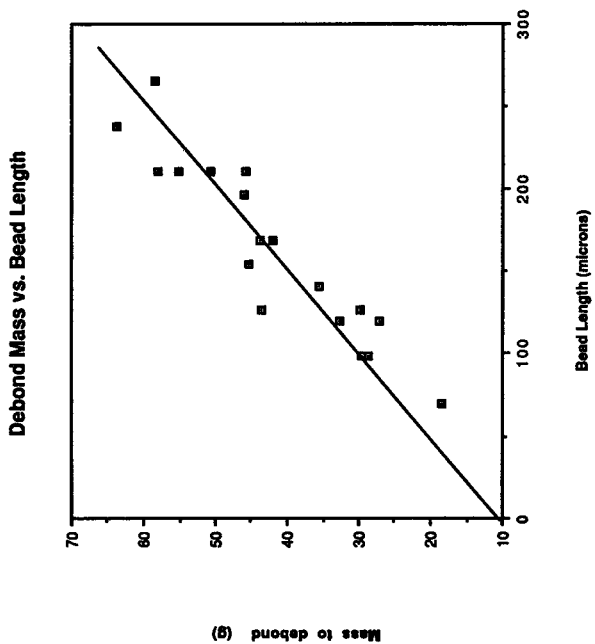
Figure 5

FIGURE 6

Interfacial Shear Strength vs.
Silane Solution Soncentration

dry
wet

Interfacial Shear Strength (MPa)

Weight percent of Silane Solution
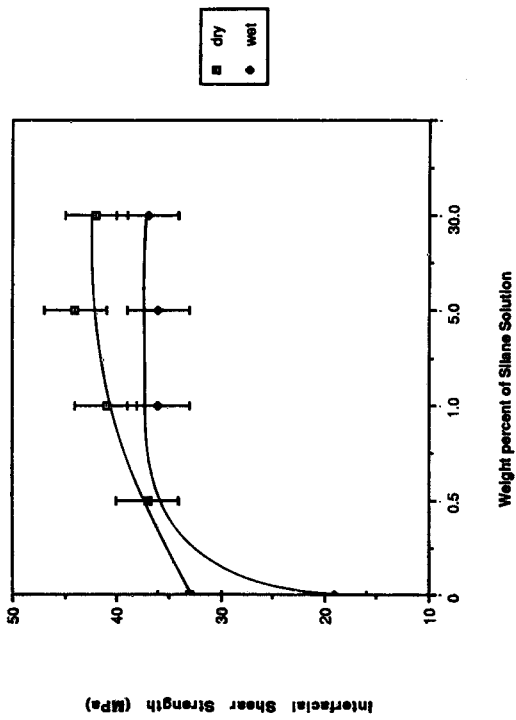
Weight % of Fiber Loading vs.
Weight % of Silane Solution.

Weight % of Silane Solution

Weight % of Fiber Loading
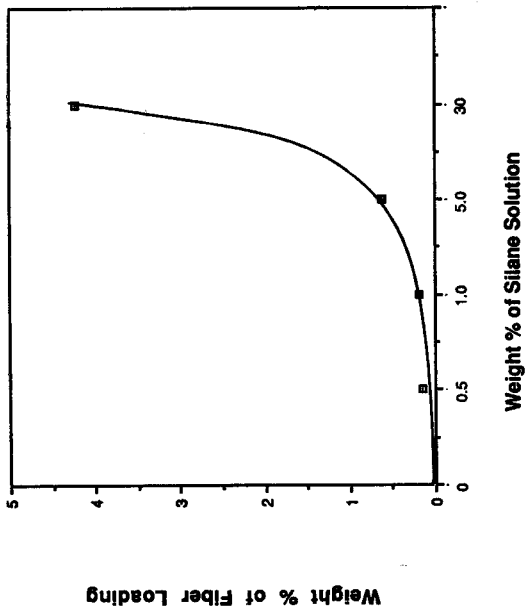
FIGURE 7

FIGURE 8

Interfacial Shear Strength (MPa) vs.
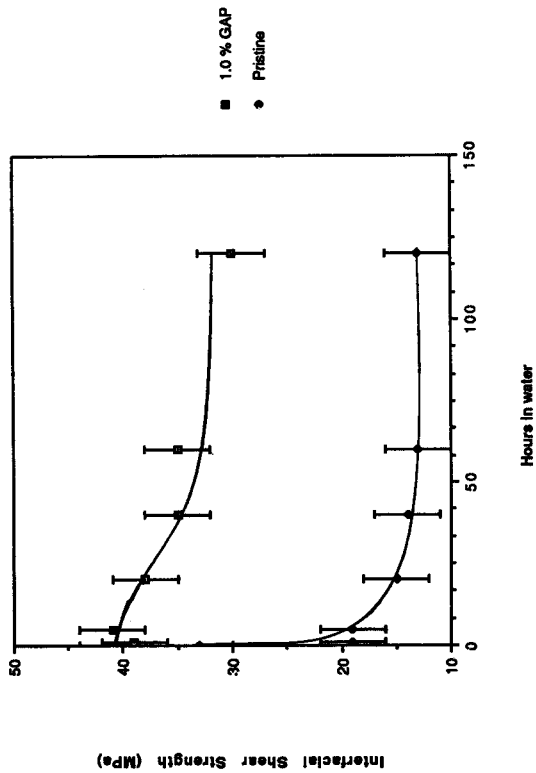Hours in water at 40 C.

■ 1.0 % GAP
◆ Pristine

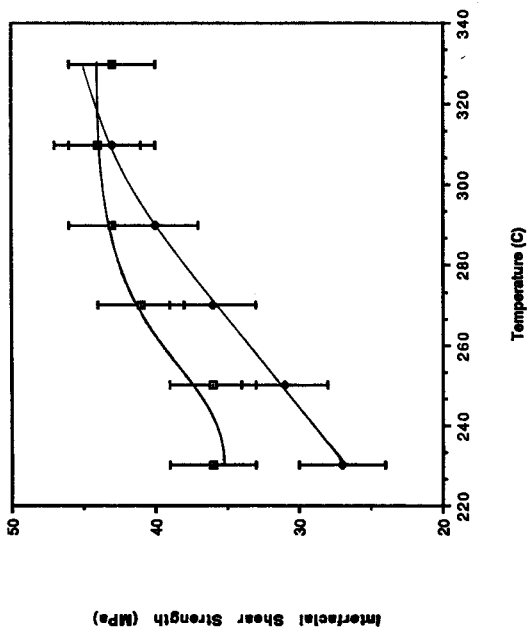Interfacial Shear Strength (MPa) vs.
Processing Temperature (C)

FIGURE 9

■ 1.0% GAP

● Lubricated Fibe

Temperature (C)

Interfacial Shear Strength (MPa)