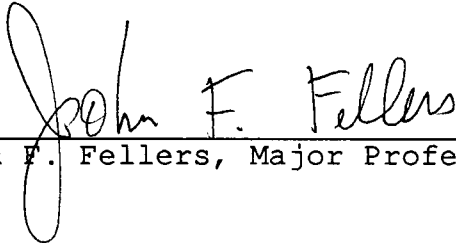


To the Graduate Council:

I am submitting herewith a thesis written by Cheol Y. Cha entitled "THE CHARACTERIZATION OF SURFACE MODIFIED GRAPHITE FIBERS/EPOXY COMPOSITES BY MECHANICAL TESTING AND SCANNING ELECTRON MICROSCOPY." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


John F. Fellers, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:


Vice Provost
and Dean of The Graduate School

THE CHARACTERIZATION OF SURFACE MODIFIED GRAPHITE
FIBERS/EPOXY COMPOSITES BY MECHANICAL TESTING AND
SCANNING ELECTRON MICROSCOPY

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Cheol Y. Cha

May 1989

DEDICATED TO MY PARENTS

ACKNOWLEDGMENTS

The author would like to express his deepest appreciation to his major advisor, Dr. John F. Fellers, for his advice and guidance throughout this research study.

Deep gratitude is also extended to Dr. A. Mathews for his help in the operation of 4-point bending tester.

The author is grateful to all of the faculty members, fellow students, workshop and office staff of the Materials Science and Engineering Department for their cooperation and assistance. Special thanks are extended to Dr. Young-Chul Lee, and Young D. Lee for many useful discussions and advice.

Finally the author is grateful to his parents for their devoted love and support.

ABSTRACT

The effect of gas plasma etched graphite fibers on the interlaminar shear strength(ILSS) of unidirectional graphite fiber/epoxy resin composites with various fiber volume fraction has been studied. The tensile properties and ILSS of composites with various fiber volume fraction have been studied using an Instron Tensile Tester. The etched surface of the fibers and the fracture surface of composites have been studied using scanning electron microscopy(SEM) .

The surprising result from the tensile tests is that the percent elongation of AS4/epoxy composites was much higher than that of individual components, i.e., the epoxy and the fiber. The stress-strain curves of AS4 fiber/epoxy composites show yielding. The yielding is interpreted to result from shear stress concentration due to the fiber breakage. Two cases of failure mode were observed in this study; i) ductile plastic deformation by the PAN-based AS4/epoxy composites, ii) brittle catastrophic failure shown by the pitch-based VSB-16/epoxy composites. The tensile strengths and moduli of the composites increased as the volume fraction of fibers increased. AS4/epoxy

composites showed greater tensile strength but lower moduli than HMS/epoxy composites.

The results of four-point bending tests showed that the ILSS of these composites did not change greatly with etching time. The values of ILSS showed a maximum about at 25% fiber volume fraction. The composites of epoxy/PAN(poly acrylonitrile) based fibers (AS4 and HMS) showed greater ILSS than those of the pitch-based fiber(VSB-16)/epoxy.

The SEM investigation on these fibers showed little change in fiber surface with 0-4 min plasma etching. The most characteristic features of interlaminar shear failure surface of AS4/epoxy composites are delamination and formation of hackles. The principal fracture features of AS4/epoxy composites under tension were fiber pull-out (bundles and single fibers) and very rough fracture surface due to the pull-out of fiber bundles with epoxy.

TABLE OF CONTENTS

SECTION	PAGE
I. INTRODUCTION.	1
II. LITERATURE REVIEW AND BACKGROUND.	3
1. Epoxy Resin.	3
1) Synthesis of Epoxides	3
2) Curing Agents of Epoxy Resins	5
3) Characterization of Epoxy Resin/Curing Agent Systems	7
2. Graphite/Carbon Fibers	12
1) Structure and Graphitization of C/G Fibers.	12
2) Comparison of PAN with Pitch based C/G Fibers.	19
3. Composites	20
1) Fracture of Composite Materials	21
2) Characterization of Composite Materials	25
4. Surface Treatments and their Effect on Composites	34
1) Theory of Adhesion.	34
2) Surface treatment of C/G Fibers	39
3) Gas Plasma Etching.	43
III. EXPERIMENTAL MATERIALS AND PROCEDURES	46
1. Materials.	46
1) Epoxy Resin and Curing Agent.	46
2) Graphite Fibers	46
2. Sample Preparation	48
1) Plasma Etching.	48
2) Preparation of Epoxy and Composite Samples.	48
3. Sample Characterization and Experimental Procedures	50
1) Density and Volume Fraction Measurement	50
2) Mechanical Test	50
3) SEM	53
IV. RESULTS AND DISCUSSION.	54
1. Mechanical Tests	54
1) 4-Point Shear Test.	54
2) Tensile Test.	65
2. SEM Studies.	81
V. CONCLUSIONS	118
REFERENCES	121
APPENDIX	128
VITA	131

LIST OF TABLE

TABLE	PAGE
1. Chemical Structures of Materials.	47
2. ILSS of AS4	55
3. ILSS of HMS	56
4. ILSS of VSB-16.	57
5. The Tensile Test.	66
6. Comparison the Tensile Strength from Tensile Test and Four-Point Bending Test.	77

LIST OF FIGURES

FIGURE	PAGE
1. The dimensions of the specimens.	52
2. ILSS of AS4/epoxy composites	58
3. ILSS of HMS/epoxy composites	59
4. ILSS of VSB-16/epoxy composites.	60
5. Comparison of ILSS at no etching	61
6. Comparison of ILSS at 2 min etching.	62
7. Comparison of ILSS at 4 min etching.	63
8. Stress-strain curves of AS4/epoxy composites . .	67
9. Stress-strain curves of HMS/epoxy composites . .	68
10. Stress-strain curves of VSB-16/epoxy composites.	69
11. Stress-strain curves of epoxy.	70
12. Comparison of stress-strain curves	71
13. Tensile strength vs. volume fraction	72
14. Modulus vs. volume fraction.	73
15. Percent elongation vs. volume fraction	75
16. Comparison of AS4/epoxy tensile strength from tensile test and from bending test	78
17. Comparison of HMS/epoxy tensile strength from tensile test and from bending test	79
18. Comparison of VSB-16/epoxy tensile strength from tensile test and from bending test	80
19. The SEM of the fracture surface of unetched AS4/epoxy composites - under bending	82
20. The SEM of the fracture surface of 2 min etched AS4/epoxy composites - under bending	84

21. The SEM of the fracture surface of 4 min etched AS4/epoxy composites - under bending	86
22. The SEM of the fracture surface of unetched HMS/epoxy composites - under bending	89
23. The SEM of the fracture surface of 2 min etched HMS/epoxy composites - under bending	91
24. The SEM of the fracture surface of 4 min etched HMS/epoxy composites - under bending	93
25. The SEM of the fracture surface of unetched VSB-16/epoxy composites - under bending.	95
26. The SEM of the fracture surface of 2 min etched VSB-16/epoxy composites - under bending.	97
27. The SEM of the fracture surface of 4 min etched VSB-16/epoxy composites - under bending.	99
28. The SEM of the fracture surface of AS4/epoxy composites - under tension	101
29. The SEM of the fracture surface of AS4/epoxy composites - under tension	107
30. The SEM of the fracture surface of VSB-16/epoxy composites - under tension	108
31. The SEM of the fracture surface of HMS/epoxy composites - under tension	114
32. The dimension of mold base	130
33. The dimension of composite sheet used.	130

I INTRODUCTION

The mechanical properties of composites depend on the intrinsic characteristics of the fiber and matrix, however, the overall performance of fiber reinforced composites is also greatly dependent on the fiber-matrix interface. The interface controls many important composite properties (e.g., ILSS). Good adhesion between fiber and matrix is a precondition for stress transfer in fiber reinforced composites.

One of the principal problems encountered in the use of new fibers in resin composites is to establish mechanical interlocking, physical adhesion and chemical bonding to achieve maximum adhesion between the resin and fiber surface. One means to achieve good adhesion in the composite is surface treatments [47,71,77,78,80,81,82] of the graphite fibers. Thus, a considerable effort was focused on surface modification via plasma etching in order to elucidate the etching effect on the interfacial adhesion between matrix and fiber.

The characteristics of stress-strain curves from tensile test, where composites were made with two different types of graphite fibers, i.e., PAN precursor and pitch precursor fibers, were investigated to study the influence

of the constituent material on the mechanical properties and on the overall crack propagation behavior of the composites.

It is the purpose of this research to modify the surface of fibers via plasma etching, to characterize the effect of the etching on the mechanical properties of uniaxial composites ranging 10-40 % fiber volume fraction using mechanical measurements, and to correlate these results with the fracture surface morphology obtained from SEM to elucidate the role of surface treatments in promoting adhesion of the interface of unidirectional graphite fiber/epoxy composites.

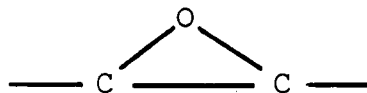
II LITERATURE REVIEW AND BACKGROUND

1. Epoxy Resin

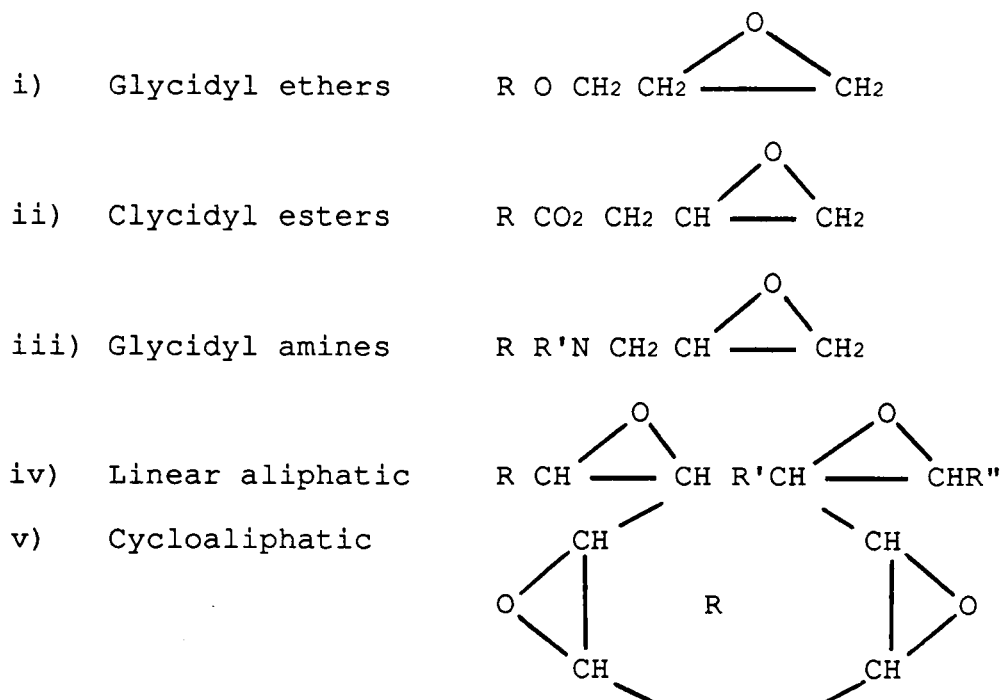
In common with phenolic and some polyester resins, the epoxy resins are thermosetting materials. When converted by a curing agent, the thermosetting resins become hard, infusible systems. The thermosetting epoxy resins possess a number of unusually valuable properties immediately amenable to use in the formulation of adhesives, sealing liquids, cold solders, castings, laminates, and coatings. The more important of these properties are i) Versatility ii) Good handling characteristics (easy cure) iii) Toughness iv) High adhesive properties v) Low shrinkage vi) Inertness (good chemical resistance) vii) High electrical insulation[3].

1) Synthesis of Epoxides

In a broad sense, epoxy refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms already united in some other way. The epoxy-resin molecule is characterized by the reactive epoxy or ethoxyline groups, which is a three-membered oxide ring.



The parent epoxy resins can be broadly classified into the following five chemical groups[4].



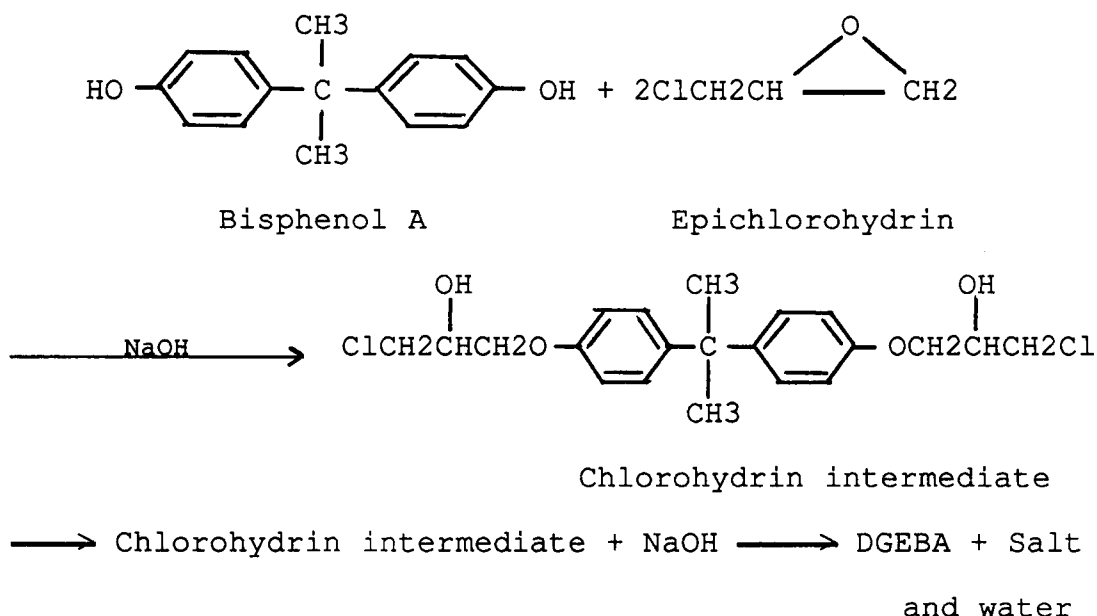
They are synthesized by various procedures. The details of their synthesis have been reviewed by Lee and Neville(2), Potter(4) and May and Tanaka[1].

The epoxide resins completely dominating world-wide markets are those based on diphenylolpropane(DPP), also known as Bisphenol A, and epichlorohydrin(ECH), and are prepared by the condensation of bisphenol A and epichlorohydrin in the presence of aqueous caustic soda at atmospheric pressure and slightly elevated temperatures[4].

The reaction occurs in two steps[2]:

i) The formation of a chlorohydrin intermediate and

ii) The dehydrohalogenation of the intermediate to the glycidyl ether.



2) Curing Agents of Epoxy Resins

One of the valuable properties of epoxy resins is their ability to transform readily from the liquid (or thermoplastic) state to tough and hard thermoset solids. This conversion from a liquid or friable brittle solid into a tough cross-linked polymer is called curing or hardening. This hardening is accomplished by the addition of a chemically active reagent known as a curing agent (or hardener or activator or catalyst).

The choice of curing agents to be used with an epoxide resin will depend upon: i) the handling characteristics

required or tolerable in the uncured system, such as viscosity at working temperature, pot life, exotherm, and toxicity, ii) the cure and post-cure time and temperature requirements, iii) the properties (physical, mechanical, electrical, and chemical) required of the cured system, and iv) the cost of the curing agent[2].

In epoxy curing systems, the curing agents fall broadly into two types[4]: i) catalytic curing agents ----> serve as initiators for resin homopolymerization. ii) polyfunctional curing agents ----> used in near stoichiometric amounts and function as reactants or comonomers in the polymerization. In most of these curing reactions the actual mechanism is ionic in nature; both anionic and cationic polymerization can occur, depending on the curing agent concerned.

Curing agents have been considered in the following broad categories[4].

- i) Primary and secondary aliphatic polyamines and derivatives. A group of unmodified room-temperature curing agents which can be regarded as having low viscosity. Polyamides are also included.
- ii) Modified primary and secondary aliphatic amines. Again room-temperature curing system, developed to improve certain characteristics such as longer pot life, faster cures, and easier handling.

- iii) Aromatic amines. Essentially hot-curing systems, offering improved heat and chemical resistance and better strength properties.
- iv) Acid anhydrides. A family of long pot-life, low viscosity and low reactivity (in the absence of a catalyst).
- v) Catalytic curing agents. Usually offer special properties, and frequently have long pot lives at room temperature.

3) Characterization of Epoxy-Resin/Curing Agent Systems

The cured-resin system is best characterized by its physical, chemical, and mechanical properties. It is clear that physical, mechanical, and chemical characteristics all stem from the basic molecular structure of the polymerized resin. Important factors at the molecular level in determining these properties are[3]:

- i) the extent of the cross-linking reaction, i.e., the degree of cure,
- ii) the cross-link density,
- iii) the nature of the resin molecule between cross-links,
- iv) the nature of the curing agent molecule.

To obtain the most favorable properties in any cured resin system it is important to achieve maximum cross-linking. A theoretical method for calculating the optimum cure cycle for a given compound has not been advanced. The

usual procedure is to determine the degree of cure empirically in terms of optimizing the desired end properties. A measure of the degree of cure is often taken to be the extent of conversion, i.e. the extent to which epoxide groups are consumed. During cure, two phenomena are involved: Conversion (the disappearance of reactive group) and, more important; cross-linking (the coupling of the molecules into three-dimensional networks through reactive sites to form the desired thermoset resins) [3].

The cross-link density in different systems depends upon the functionality of the reacting species and the distance between their groups. The nature of the resin or curing agent molecule between reactive groups, whether it is rigid or flexible, also has a direct influence on physical characteristics.

The major characterizing properties of the physical system of the cured resin are the tensile strength, compressive strength, flexural strength and modulus of elasticity.

Morgan et al. [5] revealed that the DGEBA-T403 epoxies were ductile in tension at 23°C and exhibit a macroscopic yield point, and undergo necking and plastic deformation. The plastic deformation initially occurred homogeneously, but ultimately developed inhomogeneously in the form of shear bands. They attained a maximum of 15 % tensile strain of

these epoxies for the highest crosslinked glass. They reported the density, yield stress, tensile strength, and modulus of these glasses all decreased with increasing polyethertriamine concentration as a result of increasing free volume because of poor packing ability of the amine molecule.

Kim et al.[6] examined the effect of stoichiometry on ultimate properties. They selected the system based on a bisphenol-A-type epoxy cured with methylene dianiline. The results were obtained for resins in which the amine/epoxy ratio ranged between 0.7 and 2.2. The results showed that the tensile strength, modulus, and ultimate elongation were relatively insensitive to stoichiometry but show slight maxima or minima when the amine was somewhat in excess. Impact strength and fracture toughness were, in contrast, quite sensitive to stoichiometry, increasing significantly as the amine/epoxy ratio was increased.

The effect of crosslinking density on the properties of epoxy resins has been studied mostly by varying the stoichiometric ratio of epoxy resin and curing agents in order to control the degree of crosslinking[5,6,7]. Chang et al.[7] found the bulk density increased linearly with the crosslinking density. Also the modulus and the yield point of a deformed sample all increased with the degree of crosslinking. The increase of the density with the extent

of curing suggested that the free volume in the epoxy resins was reduced by the crosslinking. The crosslinking might also contribute to an increase of modulus by adding stronger chemical bonds.

Epoxy resins are prone to crack propagation sometimes by means of a stable(continuous) mode and at other times by means of a unstable('stick-slip') mode[8, 9]. Yamini et al.[8, 9, 10] showed that the stability of crack propagation in an epoxy resin was governed by the type of curing agent employed, temperature, rate of testing and environment. The cracks in epoxy resins were found to propagate in an unstable 'stick-slip' manner at high temperatures and with low rates of testing whereas at lower temperatures and using higher rates of loading propagation was more stable and cracks propagated in a continuous manner.

Yamini and Young[11] measured the yield stress and Young's modulus of epoxy resins as a function of resin composition, testing rate and temperature. They found that for a given composition, both yield stress and Young's modulus increased as the testing rate was increased and as the temperature was decreased. They also found that under the same testing condition, yield stress and Young's modulus both decreased as the amount of curing agent in the resin was increased.

Tang et al.[12] investigated the effect of cure pressure on voids and mechanical properties. Pressure was applied to squeeze out excess resin and to minimize void content. The results showed that the cure pressure influenced the void content, in turn, the void content affected the mechanical properties, especially interlaminar shear property. The data showed that below a critical void content level, the void content did not affect significantly the interlaminar shear property, suggesting that it is not imperative to eliminate all the voids from the composite.

Morgan and Walkup[13] evaluated the five epoxy-curing agent systems suitable for filament-wound carbon fiber composites. In order to efficiently impregnate the fiber bundles epoxy resins must exhibit low viscosities and long gel time at room temperature. These required a flexible amine molecule. The flexibility of amine curing agent allowed utilization of low post-cure temperature, $<150^{\circ}\text{C}$, which resulted in minimizing the development of fabrication strains in the composite. From the experimental data, they concluded the DGEBA - DMHDA(2,5-dimethyl-2,5-hexane diamine) epoxy system offered the best potential as a filament-winding resin for carbon fiber-epoxy composites.

Epoxies observed from fracture topography[14,15] failed by void growth and coalescence through a simultaneously growing craze. Heterogeneties in the 10 to 60 nm size range

have been identified in the cured epoxy resin[14,16,17]. Gupta et al.[17] observed the size of the heterogeneity was a function of curing agent concentration and also of cure cycle.

By synthesizing a series of diglycidyl ethers from new bisphenols containing different numbers of oxyethylene units in the molecule, Kakiuchi et al.[18] studied the effects of chemical structure of the cured resins on their mechanical, electric and adhesive properties. The results showed that the incorporation of oxyethylene segments ($-O-CH_2-CH_2-$) into the network resulted in an increase in the flexibility and polarity of the cured resins. The enhancement of the polarity of the cured resins resulted in the increase in the electric constant and tensile shear strength.

2. Graphite/Carbon Fibers

Carbon/Graphite(C/G) fibers are high strength, high modulus, lightweight fibers which are the predominant reinforcement in advanced composites today. They are attractive fibers for use in high performance applications such as primary aircraft structures.

1) Structure and Graphitization of C/G Fibers

C/G fibers can be produced in a large number of ways. The industrially convenient methods, though, are restricted

to those using thermal oxidation and graphitization of organic precursors. The process is based on three steps[20]:

- i) low temperature oxidation, in air at 200 - 300 °C
- ii) carbonization stage in inert atmosphere at about 1000 °C,
- iii) graphitization stage in inert atmosphere at temperatures over 2000 °C.

Graphitization is the process by which randomly stacked, defective graphite sheets are converted into more perfectly stacked(defect-free) graphite. The process takes place simply by heating to temperatures above 2500 °C. Graphitization proceeds from the outside of the fiber inward. However, in polymeric carbons, because of the short distance between boundaries, the boundary restraint is extremely great, and so perfect stacking does not occur.

Today's graphite fibers are prepared from either organic fiber precursors or pitch via a pyrolysis-type process. Much of the early work was performed using rayon precursors[27,30]; however, rayon soon gave way to polyacrylonitrile(PAN) which has become the predominant organic precursor fiber.

Broadly speaking, the fibers fall into three groups which depend on the modulus: i) low modulus, high strength fiber with a modulus of about 240 GPa, ii) high modulus

material in the range 350-450 GPa, and iii) very high modulus fiber with a modulus of about 800 GPa[24].

Many different processes have been used to convert PAN fibers into graphite fibers. However, the general process consists of four major steps[19,25].

- i) PAN fiber preparation - special grades of PAN fiber are produced. These fibers are subjected to a stretching operation which orients the fibrillar structure of the PAN and improves its mechanical properties.
- ii) Stabilization - a process in which the PAN is stabilized against polymer relaxation or softening during subsequent elevated temperature processing steps. The oriented PAN is typically stabilized under tension in an oxidizing atmosphere.
- iii) Carbonization - the process by which the stabilized PAN is pyrolyzed into carbon fibers. This process is carried out in an inert atmosphere at temperatures of 1000-1500 °C. Tension may be employed to achieve higher degrees of orientation.
- iv) Graphitization - the highest temperature step, on the order of 2500-3000 °C, in which a higher carbon yield and more graphitic microstructure are obtained than in the carbonization step. Tension may be employed in this step to achieve higher degrees of preferred orientation in the fiber. Higher degrees of orientation typically provide

higher moduli. Depending on the specific conditions employed in each step, graphite fibers can be produced having a wide range of properties.

The process of making graphite fibers from a pitch precursor typically consists of the following steps[19,25]:

- i) conversion of the pitch to a mesophase pitch. Pitch is heated in an inert atmosphere for an extended period of time. During this heating, amorphous pitch is transformed into a highly ordered, liquid crystalline state-mesophase pitch.
- ii) Spinning mesophase pitch into fibers - a melt spinning process in which the liquid crystal pitch is extruded through a die to produce fibers.
- iii) Stabilization - a process similar to that described for PAN. Oxidizing atmospheres or liquids are used.
- iv) Carbonization - a process similar to that described for PAN.
- v) Graphitization - also a process similar to the PAN process.

While steps 3,4, and 5 are similar to the PAN process, specific conditions tailored for a pitch process would be used. As with the PAN fibers, conditions can be varied to give a variety of fiber properties.

The basic structure of the PAN-base carbon fibers[26] and rayon-base fiber[27] is the ribbon of SP^2 carbon aligned axially. The average width of these ribbons is in the 50-70 Angstroms and the length is in several thousand Angstroms.

The variation in these structural elements depends on the graphitization temperature and processing of the particular fiber.

The high mechanical properties achieved with graphite fibers are attributable to the structure and orientations of the graphite crystals formed during processing. High strength, high modulus carbon fibers are about 7-8 μm in diameter and consist of small crystallites of "turbostratic" graphite. In a graphite single crystal the carbon atoms are arranged in hexagonal arrays. The atoms in the layer or basal planes are held together by very strong covalent bonds and there are weak van der Waal forces between the layer. These planar layers are oriented in the direction of the fiber axis as a result of the fiber processing steps. Varying degrees of orientation result in variations of fiber properties, particularly fiber modulus[37].

The X-ray diffraction pattern of a bundle of PAN fibers heated to 200 $^{\circ}\text{C}$ was of the fiber structure similar to that of the original PAN. The pattern of a fiber bundle heated to 300 $^{\circ}\text{C}$ contained that of carbon, and a fiber bundle heated to 400-1000 $^{\circ}\text{C}$ gave patterns indicating the presence of polynuclear aromatic fragments whose ring planes are oriented parallel to the fiber axis[22].

When carbon yarn is graphitized, the internal structure becomes highly textured. A well-defined pore structure

develops. The graphitization process results in a reduction in the number of small pores present in carbon fibers and the development of larger pore sizes. As these larger pores are formed, they also become closed. This pore structure has been studied quantitatively and in detail by small angle X-ray scattering techniques by Perret and Ruland[28].

They[29] also demonstrated the microstructure of PAN-base carbon fibers was essentially the same as that of rayon-base carbon fibers. A difference appeared only in the volume fraction occupied by the voids, which was considerably lower in the PAN-base fibers than in rayon-base fibers.

Carbon/graphite fibers from pitch have a more uniform cross section than those from other precursors, as the pitch products have had significant processing to remove volatile matter before the extrusion operation to yield fibers with higher density and carbon content. Fibers having a carbon content greater than 98% are obtained by carbonization in an inert atmosphere at temperatures in excess of 1000°C.

Carbon fibers produced in this manner have a highly oriented structure characterized by the presence of carbon crystallites aligned parallel to the fiber axis. Further graphitization at temperatures above 2800°C develops the three dimensional order characteristic of polycrystalline graphite. Wick and Coyle[29] distinguished two distinct regions in fibers heat-treated at 2500 °C, namely i) an

inner region, or core, characterized by relatively low axial alignment and large crystallite size, and ii) an outer sleeve, or sheath, of material of high axial preferred orientation and low average crystallite size. The relative amounts of "sheath" and "core" in fibers of different diameter affected the Young's modulus and tensile strength of graphite fibers made from PAN and rayon precursors[30].

Barnet et al.[31] proposed a 3-D structural model for high modulus PAN-based carbon fibers. This model included the more highly crystalline parts of the fiber: a surface sheath, a core section, and a number of webs running radially between the core and sheath. Also present were internal voids, flaws, residual stresses, and cracks, as well as flaws on the fiber surface. The sheath had a continuously undulating, long-range crystalline structure, with the basal planes running parallel to both the fiber axis and circumference. The core was apparently highly crystalline and possibly as well as ordered as the sheath.

Dorey[32] examined carbon fibers by X-ray diffraction and by transmission electron microscopy. The results indicated that they had a kind of fibrillar microstructure, related to the interlocking fibrils in the spun PAN fibers but more firmly stuck together. The fibrils and carbon layer planes within them were preferentially aligned along the fiber axis. Although the carbon layers consisted of

hexagonal carbon rings like graphite and had approximately the same spacing, there was no ABAB stacking sequence order. The structure was turbostratic.

Bennett et al.[33] observed that internal flaws, which did not initiate failure, were seen to have walls containing crystallites arranged mainly parallel to the fiber axis, and internal and surface flaws which did initiate failure showed evidence of large misoriented crystallites in the walls of the flaws. They concluded that the presence of misoriented crystallites rather than the flaw itself determined whether tensile failure would occur or not.

The moduli of individual fibers depend on the preferred axial orientation in each fiber structure, on the other hand the strength is a function not only of preferred orientation but also of the flaws and the textures in structure present[34].

2) Comparison of PAN with Pitch Based C/G Fibers

When drawing comparisons between the manufacturing methods for PAN based carbon fibers and pitch-based carbon fibers, there are advantages in favor of the latter. The carbon yield from mesophase pitch is about 75% to 85%, whereas the yield from PAN is only about 50%. Because the as-spun pitch fibers are highly anisotropic, there is no

need to apply tensioning during the oxidative treatment, and carbonization may be carried out at a rapid rate[36].

Bell and Perry[35] evaluated composites using C/G fibers from pitch and PAN sources. Tests included mechanical properties in dry and wet conditions at room and elevated temperatures. They concluded that epoxy composites prepared with pitch/graphite fibers were suitable for stiffness critical applications, but flexural, tensile, and compressive strengths were lower than for those composites prepared from HM-S fibers from PAN precursors. HM-S graphite fibers yielded higher flexural strengths and higher interlaminar shear strengths in the composites than pitch origin fibers. While pitch-based graphite fibers have attained moduli in excess of 100×10^6 psi, this has been accomplished at some sacrifice in tensile strength and impact resistance.

Most of the high strength fibers are made from polyacrylonitrile and tend to have lower moduli. Continuous pitch-based fibers are generally in the high modulus region but of low strength.

3. Composites

A composite is formed when two or more materials are judiciously combined, usually with the intent of achieving better results than can be obtained by using the individual

materials by themselves. This simple concept has wide implications, as it introduces new ways of planning the development and application of materials. Three main points are included in a definition of an acceptable composite material for use in structural application. i) it consists of two or more physically distinct and mechanically separable materials. ii) it can be made by mixing the separate materials in such a way that the dispersion of one material in the other can be done in a controlled way to achieve optimum properties. iii) the properties are superior, and possibly unique in some specific respects, to the properties of the individual components[37].

C/G fiber composites have an organic resin binder, or matrix, to weld them into a solid body. The carbonaceous fiber portion contributes stiffness and strength, a large reduction in thermal expansion coefficient, a large improvement in fatigue strength, and decreased electrical resistivity. The technology of C/G composites entails examination of how to combine such diverse materials into useful engineering products, using different resin materials, and hybridization with other fibers.

1) Fracture of Composite Materials

Current research efforts on advanced composites may be broadly classified into: i) mechanical responses, such as

deformation processes without any damage considerations, and ii) detailed studies of various failure modes that occur in the composite during application of stress. It should also be remembered that stresses which arise may not only be applied externally (mechanically or even electrically), but also may be applied from internal considerations due to differences in thermal properties of the composite components. More knowledge of material damage at the microscopic level is needed. This will assist understanding of the various modes and of the way in which physical damage such as micro-cracking, affects the overall behavior of the composite. Today we recognize that the onset of fracture instability is the result of interaction of the crack driving force and the crack resistance of the material. When the crack driving force equals or exceeds the crack resistance, instability ensues[36].

Of particular importance is the role of the matrix and the interface in isolating individual fiber fractures by inhibiting the formation of a single crack, which will contribute to composite failure. Mullin[39] studied the influence of fiber property variations and drew the following conclusions: i) reinforcing C/G fibers are the primary load carriers and their strain energy density and volume fraction are critical parameters in the energy per unit volume of composite to initiate cracks. ii) there are

distinct changes in local fracture modes when surface treatments are applied to the fibers[39].

In order to study the mechanism of fiber-matrix adhesion, Drzal et al.[40] developed a simple single filament technique which relies on determination of fiber critical length combined with polarized light microscopic observation of the fiber-matrix interface under stress.

Drzal et al.[40,41,75] studied reinforced fibers not only with surface treatments[40,75] to increase the chemical interaction between fiber and matrix but also with surface finishes or sizing[41] applied to enhance compatability with the host matrix. They[40,41,75] found a two-fold effect of the application of a resin finish to graphite fibers, i) there is an increase in the interfacial shear strength between fiber and matrix, ii) the mode of failure at the fiber break is altered from growth of an interfacial crack between fiber and matrix to that of a matrix crack perpendicular to the fiber axis.

Manocha et al.[42] observed the following results. i) the composite with surface treated carbon fiber showed quite strong fiber/matrix interactions and resulted in catastrophic failure of the composite with low strength. ii) whereas those with non-surface treated fibers showed relatively weak fiber/matrix bonding and resulted in pseudo-plastic failure with high strength.

Sharp, crack-like flaws in fiber composite structures may be present for many reasons, ranging from material irregularities, improper fabrication, and adverse environmental exposures to in-service damage of the structure. One of the purposes of fracture mechanics is to study such flaws and to determine how to design and apply advanced composites so that the appearance of flaws is minimal, and if they occur, for whatever reason, to suggest measures to contain the flaws and avoid rapid and catastrophic failures.

The fracture process generally takes place in three stages[38]. i) a microcrack is initiated (or an initial flaw or imperfection can be present). ii) the microcrack grows in a stable fashion and may link with other microcracks to attain macrocrack size. iii) the macrocrack propagates in an unstable fashion at a critical stress level. These three stages are found and clearly defined only in ductile materials. Some of the stages, for example, stage two, are not found in brittle materials. A prominent characteristic of composite materials is their high resistance to crack propagation because of the matrix ductility.

Fracture is caused by higher stresses around flaws or cracks than in the surrounding material. However, fracture mechanics is much more than the study of stress

concentration factors. Such factors are useful in determining the influence of relatively large holes in bodies, but are not particularly helpful when body has sharp notch or cracklike flaws. For composite materials, fracture has a new dimension as opposed to homogeneous isotropic materials because of the presence of two or more constituents. Fracture can be a fracture of the individual constituents or a separation of the interface between the constituent.

2) Characterization of Composite Materials

The interface controls most of the mechanical properties of the composites, e.g. strength, Young's modulus, etc., because stress transfer between the matrix and the fiber, which normally carry most of the load, takes place there. Two extreme cases are generally encountered in interfacial failure mode ----- poor interfacial bonding and strong interfacial bonding. In the case of poor interfacial bonding, fiber pull-out is observed. This is indicated by poor mechanical properties. If the interfacial bonding is strong, then effective load transfer is achieved and good composite properties are measured. However, this also means that the composite is brittle and failure is usually sudden and catastrophic.

Novak[43] studied the mechanism of failure in graphite filament reinforced epoxy composites under shear loading. He observed: i) at low interfacial strength, failure was progressive, initiating at the interface and propagating from filament to filament, ii) as interfacial strength was increased by filament treatment, failure occurred at the interface and in the matrix and tended to be increasingly brittle, iii) at high interfacial strength, composite shear strength was high, but failure could be very brittle, this means that increasing the shear strength may be detrimental to other composite properties such as impact strength[43,44]

Mizutani and Iwatsu[45] investigated the fracture behavior of composites consisting of a single carbon fiber(CF) tow in thermosetting resins. The results showed that as the CF composites were tensioned in the fiber direction, a failure of the CF composites was initiated by the fracture of the carbon filaments and a crack propagated into the resin matrix from the CF.

However, in the Lee et al.[46] studies of the dynamic small angle x-ray scattering studies on the unidirectional Kevlar 49 fiber reinforced epoxy composites of low volume fraction, the results showed the failure as a catastrophic dynamic process, the crack originating from surface flaws or air bubbles entrapped in the epoxies during the curing process.

Interfacial bond strength and failure mechanism were studied by single-filament critical length determination[40]. Ying[47] obtained good correlation between single filament critical length shear strength determination and composite short beam shear strength. He concluded that the single filament critical length shear strength determination is a good test to characterize carbon fiber/epoxy adhesion properties and inherent failure mechanism.

Using carbon fiber-reinforced epoxy resin samples made with aligned fibers, with lengths of 1 to 5 mm, Sanadi and Piggott[48] observed that strengths and Young's moduli were affected by fiber length and fiber volume fraction. The results showed that the strengths of the composites increased monotonically with fiber volume fraction and the Young's moduli of the 2 and 5 mm fiber composites were linear functions of fiber volume fraction.

Sato et al.[49] studied the influence of small diameter fibers on the mechanical properties of the short fiber composite. They found that the composite strength and toughness were increased as the fiber diameter became smaller than the conventional one. They considered the following factors as the reinforcing mechanism; i) enhancing the stress transfer through the interface, ii) reducing the degree of the stress concentration at the fiber end, iii)

increasing the crack path length, iv) increasing the region of the plastic deformation of the matrix.

Kline and Chang[50] examined the fracture surfaces of graphite-epoxy composites by using SEM. Specimens were loaded to failure in tension, tension-tension fatigue and compression. They observed hackles(lacerations), overlapping platelets of epoxy, and cleavage-like microcracks which branch near fiber-epoxy boundaries. Extensive surface hackles were formed due to delamination as a result of compression loading. These features could be used to identify the direction of failure propagation and, in some case, distinguish failure modes.

The crack propagation behavior of a composite material depends on the mechanical properties of the constituents, the bonding of the matrix with the filler, the loading conditions and some other parameters, such as temperature, humidity, etc.

Sato et al.[51] investigated the fracture mechanism of unidirectional carbon-fiber reinforced epoxy resin composite by a 3 point bending test. They showed the failure process to proceed through the following four stages: i) fiber breakage began to occur at a load of about 60% of the failure load, ii) as the applied load was increased, plastic deformation occurred first from the broken fiber tip along the fiber sides, followed by final matrix cracking in

the plastic region, iii) just before failure, partial delamination occurred, originating from fiber breakage and matrix cracking, iv) finally, a catastrophic crack propagation occurred from the delamination, leading to composite failure.

Theocaris et al.[52] studied the mode of crack propagation by means of a Scanning Electron Microscope (SEM). The composite specimens used were composed of an epoxy polymer matrix reinforced with unidirectional carbon fibers. As regards the crack propagation in the composites, they[52] derived the following results from the observation of fracture modes of these specimens. i) initially, the crack propagates in a self-similar manner into the matrix. When it arrives at an interface, then it continues its propagation along the interface, up to fracture of the fiber, ii) after the fracture of the fiber the crack propagates again in a straightforward manner into the matrix, it follows the next interface and so on, up to the complete fracture.

Bradly et al.[53] found the fracture process and resultant fracture toughness for delamination of graphite/epoxy composites to be sensitive to the following factors: i) resin toughness, ii) interfacial strength, and iii) thickness of resin-rich region. They[53,54] observed a much larger region of damage above and below the main crack

front for graphite/epoxy composites with ductile matrix resins than for brittle matrix resins.

Bascom et al.[55] examined the failed surfaces of carbon fiber composites after mode I delamination. The principle fractography features were fiber pull-out (bundles and single fibers), hackle marking, and regions of smooth resin fracture.

Richards-Frandsen et al.[56] examined the delamination failure planes of graphite/epoxy composites under three-point bending fatigue microscopically to identify and relate fracture surface morphology to the composite microstructure and the applied loading conditions. The results showed the dominant failure surface features were matrix cleavage, hackle formation, and wear regions. No indication of crack propagation from manufacturing induced defects was observed. Instead, the role of intrinsic defects on fatigue lifetime seems to be one of damage enhancement around the defect.

The interlaminar shear strength(ILSS) of unidirectional fiber reinforced composites is often measured in the short beam shear test, ASTM Test for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short-Beam Method(D 2344-84) [57]. The simplicity of the test method makes it a very popular materials screening tool. Shear strength determined by this test method is useful for quality control and specification purposes. Unfortunately, this test

suffers from two significant limitations that seriously impair its ability to yield meaningful results. The apparent shear strength obtained in this test method can not be used as a design criteria, but can be used only as a screening test and as a quality control tools[58,59]. The test can also be utilized for comparative testing of composite materials, if all failures are in horizontal shear. The second limitation on the short-beam shear method in conjunction with unidirectional composites such as graphite/epoxy composites is that the test does not usually yield interlaminar failure.

Whitney and Browning[58] examine the interlaminar beam tests in the form of three point experimentally. Experimental data are obtained on unidirectional composites. The results show that apparent interlaminar shear strengths depend on specimen geometry. Complex failure modes in the presence of extremely high combined stress gradients are observed. In particular there is evidence that compression stresses in regions where high shear-stress components exist tend to suppress interlaminar shear failure modes. Thus, initial damage in the form of vertical cracks appears to be necessary in order to induce mixed-mode horizontal, interlaminar failures. For specimens without initial damage, the failure mode is essentially compressive buckling

or yielding in the upper portion of the beam under combined compression and shear.

The short-beam shear test for interlaminar shear strength does not yield the desired shear failure mode consistently. Thus, an alternative test method, the four-point shear(FPS) test has been developed for the desired interlaminar shear failure mode in thin-beam specimens of graphite/epoxy[60,61].

Apparent shear strength can be calculated from the classical beam relation[57,58,60].

$$S_H = 0.75 P/bh \quad (1)$$

where S_H = maximum interlaminar shear strength.

P = maximum load.

b = specimen width.

h = specimen thickness.

Equation (1) is applicable to both three-point and four-point flexure specimens.

When a composite with a continuous fiber is subjected to external loads, the fiber and matrix deform together. As the external load is increased, the stress in the fiber will be built up to fracture at the weakest point along its length. For a material reinforced with fractured and discontinuous fibers the load can be transmitted to the fiber by means of shear stresses at the fiber/matrix interface. When the external load is further increased, the

subsequent fiber fracture occurs at the second weakest point. Thus, the fiber continues to fracture in turn with an increasing external load until the fiber reaches a critical length given by

$$L_c = r\sigma_f/S_H$$

where σ_f = the average fracture strength of the fiber.

r = the radius of the fiber.

S_H = the shear strength at the fiber/matrix interface.

Thus, the shear strength at the carbon/epoxy interface can be evaluated by a critical length of the fractured fibers[63].

Mijovic[64] examined the relationships between processing and properties of graphite/epoxy composites. Different heating rates, between the common initial and final stages of cure, had an effect on physical/mechanical properties of composites. The faster the heating rate, the smaller the total amount of heat evolved during cure, i.e., the lower the extent of conversion (or crosslinking). He found that the slower the heating rate, the higher the T_g . An increase in T_g as the heating rate was decreased is explained by the increase in the number of crosslinks in the epoxy network. This effect, however, was erased by a post-cure treatment.

Harper et al.[65] investigated the effects of voids on the mechanical properties of AS4/3502 graphite/epoxy. The presence of voids resulted in a significant reduction in the transverse modulus E_{22} and shear modulus G_{12} while practically no effect of voids was observed for the longitudinal modulus E_{11} .

Chang et al.[66] studied the effect of a polymeric interlayer of a graphite/epoxy composite on the composite mechanical properties. The mechanical properties of the composites varied with the thickness and modulus of an interlayer placed at the fiber/matrix interface. They found: i) when a very thin interlayer was applied, the ILSS is at its maximum, and the impact resistance reached its minimum. ii) the shear strength dropped as the interlayer thickness increased, and this rate of decrease was inversely proportional to the modulus of the interlayer. iii) when the interlayer thickness was approximately 0.12 microns, the impact strength reached a maximum.

4. Surface Treatments and Their Effect on Composites

1) Theory of Adhesion

One of the principal problems encountered in the use of new fibers in resin composites is to establish an active fiber surface to achieve maximum adhesion between the resin

and fiber surface. The general requirements for good adhesion are that: i) the adhesive must wet the adherend surface to obtain complete and intimate contact, ii) the adhesive must become viscous or solidify during the bonding stage, and iii) the adhesive must be able to deform during solidification to relieve internal stresses caused by thermal and cure shrinkage. These requirements necessarily place conditions on the surfaces to be bonded. The condition required for wettability of the surface by the adhesive is that the surface energy must be greater than the adhesive surface energy. The second condition is that it would be desirable to have a large interfacial area of contact whether the adhesive bond is due to van der Waals physical adsorption forces or to chemical bond formation[67].

It has been well documented[68] that the fiber resin interface is the most sensitive region in a reinforced plastic. Mechanical stiffness mismatches as well as differences in thermal expansion coefficients between the two components result in stress concentrations which in turn can lead to the initiation of cracks within the composite. Interfacial voids also give rise to stress magnifications in a reinforced material, again increasing the likelihood of failure initiation.

The primary loss of strength is due to failure of the molecules to approach their proper bonding distances of a few angstrom units. One may visualise this as a microvoid at the interface which is then capable of concentrating stress and causing premature failure. A second major loss in bond strength comes about from the development of residual stresses at the interface. Normally, a matrix or adhesive is applied in the fluid state and then solidified by cooling and/or chemical reaction. This invariably causes a differential shrinkage at phase boundaries that leads to undesirable stress concentrations.

Dibenedetto and Nicolais[69] discussed the flexible interlayer concept which allows stress relief in the interphase region. Since there is a difference in thermal expansion coefficient of the fiber and the matrix, significant residual stress will accumulate at the interface due to elevated temperature curing as well as shrinkage of the matrix during polymerization. Incorporation of a flexible interlayer may relieve some of this residual stress.

A variety of theories have been developed to correlate adhesion at a fiber/resin interface with the mechanical response of the composite. The adhesion theories that have been proposed may be divided as follows[37,69,70,71].

i) The absorption theory of adhesion: This theory proposes that, provided sufficiently intimate intermolecular contact is achieved at the interface, the materials will adhere because of the surface forces acting between the atoms in the two surface; the most common such forces are van der Waals forces and are referred to as secondary bonds.

Chemisorption may well occur and thus ionic, covalent and hydrogen bonds may operate across the interface; these types of bonds are referred to as primary bonds.

ii) The diffusion theory of adhesion suggests that adhesion of high polymers is due to the diffusion of long chain molecules or their individual segments into the substrate.

iii) The electronic theory of adhesion. If the adhesive and substrate have different electronic band structures there is likely to be some electron transfer on contact to balance Fermi levels which will result in the formation of a double layer of electrical charge at the interface. The electrostatic forces arising from such contact of junction potentials may contribute significantly to the intrinsic adhesion. Adhesion is presumed to be due to the existence of these attractive forces across the electrical double layer.

iv) The mechanical interlocking. There are several ways that two materials can interact across a phase boundary. The two most important types of bonding action can be

classified as mechanical interaction and chemical interaction. A mechanical interaction can be a geometrical effect where there is an interlocking of the two components across an interface. This type of action can be important when one of the substances is porous and the other can penetrate the pores and solidify. A second type of mechanical interaction depends on a frictional resistance due to squeezing one component around an inclusion of the other.

It is reasonably well accepted that if one wishes to have interfaces that are at least as strong as the constituent materials in shear, it is necessary to develop some kind of chemical bonding. Chemical bonding at an interface is developed by wetting the solid surface with a fluid. Once molecular contact has been attained, the two phases can interact through intermolecular forces. The magnitude of the interaction depends on the type of chemical bonds formed. Chemical bonding can be classified into primary and secondary bonding. Primary bonding can be either ionic, covalent, or metallic. Secondary bonding arises from electrostatic and inductive interactions between charges, dipoles, and multipoles in adjacent molecules or from van der Waals forces between molecules[20].

An adhesive bond achieves its strength from the combination of a variety of sources; the adsorption

interactions including dispersion forces, acid/base electron donor/acceptor forces and chemical bonds; mechanical interpenetrations which depend on topography, flow and diffusion. For these various mechanism, none of the accounts of the mechanism of adhesion has any resonable claim to covering all the situations[71].

2) Surface Treatment of C/G Fibers

(It is accepted that good bonds between fiber and resin are essential to achieve good performance of the composites under adverse envirommental conditions. Too often, the resin matrix does not fill completely all the crevices and pores on the surface, including the interfibrillar crevices in fiber-reinforced composites. The presence of only partially filled surface pores and crevices contributes a significant loss of strength and moisture resistance in the composite material. One objective of surface treatments is to offset or compensate for these situations, either through chemical or mechanical means.) *generally*

Heat treatment through graphitization removes organic material, requiring surface treatments to enhance subsequent handling and resin adhesion qualities, with fibers derived from synthetic fiber precursors as well as pitch fibers. However it should be noted that the possibilities of chemical bonding to carbon surface offer more prospects for *after heat treatment*

good adhesion than with glass fibers, particularly if the oxidation treatment has developed functional bonding sites for the synthetic resin matrices used with the carbon fibers.

The adhesion of polymers, such as polyesters, epoxies, and polyimides, to the surfaces of high modulus C/G fibers is generally weak, and the surface treatment of the carbon fiber resulted in increasing the active oxygen content[72,73], the polarity[74,75], and the total free surface energy[75,76] of the carbon fiber surface by introduction of functional groups, such as hydroxyl, carboxyl, and lactone.

Surface treatments are employed to increase the interfacial bond strength of the C/G fiber composite[47,77,78,80,81,82]. Surface treatments designed to promote adhesion to epoxy matrix materials were operated through a two-part mechanism[77]. i) the treatments removed a weak outer fiber layer initially present on the fiber. ii) surface chemical groups were added which increase the interaction with the matrix.

Fitzer and Weiss[79] performed oxidative surface treatment on a laboratory scale with the wet method (boiling nitric acid), the dry method(oxidation in air) and with the anodic oxidation(in aqueous sulphuric acid). All these treatments formed surface oxides and the improved adhesion

was caused by the chemical interaction between these surface oxides and reactive groups of the matrix resin. Both the amount of surface oxides and the BET surface area were increased by extended oxidation. The fiber strength, however, was decreased because of oxidative degradation. The improvement of ILSS can be well correlated with the increasing amount of surface oxides[79,80].

Harvey et al.[81] treated surface of carbon fibers anodically by passing them through an electrochemical bath and tested their ILSS. They observed the rise in ILSS with surface treatment which was not dependent on the amount of carboxyl functionality present on the surface. Thus, they supported the view that mechanical keying of the resin to the fiber surface played an important role in forming the fiber-resin bond.

Kaplan et al.[82] treated Spectra^R fiber with plasma and found a four fold increase in ILSS over untreated fiber in fiber/resin composites. They believed the major mechanisms which were responsible for the improvements in ILSS were improved wettability, mechanical interlocking on the microscopic scale, and bonding with plasma surface treatment.

Kalnins[83] in a review of graphite fiber surface treatments proposed that the surface oxidative treatment processes i) can be carried out by means of inexpensive

commodity chemicals, ii) removes the original weakly bonded layer of surface carbon, and iii) reacts with the surface carbon to form several types of oxygen-containing groups, some of which are strongly chemisorbed to the surface carbon atoms and serve as the bonding sites for the polymeric binder.

Manocha[84] investigated the effect of surface treatment of carbon fibers with concentrated as well as dilute nitric acid on the mechanical properties of carbon fibers. For the initial treatment, the surface flaws are removed and the fiber surface is smoothed, resulting in an increase in tensile strength of the carbon fibers. Prolonged treatments with both concentrated and dilute nitric acid cause etch pits on the surface which account for the drastic decrease in strength of the carbon fibers.

Sizing for resin Experiments were carried out to evaluate the effect of cure and sizing[41,85] on the bond strength between graphite fiber bundles and epoxy resins. Peters et al.[85] drew the following conclusions: i) the cure temperature, the degree of cure, affected the mechanical properties of resins, the fiber bundle-resin bond strength, ii) sizing affected the fracture strain of specimens containing fiber bundles in two ways; first, sizing increased the bond strength between the fibers and the matrix, thereby increasing the fracture strain, second, sizing increased the fiber density inside

the bundle, thereby reducing the fracture strain. Thus, the measured fracture strain was due to a combination of these two effects.

3) Gas Plasma Etching

A gas plasma is defined as "a collection of charged particles containing about equal numbers of positive ions and electrons and exhibiting some properties of a gas but differing from a gas in being a good conductor of electricity and in being affected by a magnetic field." [Webster's dictionary] It is often referred to as the fourth state of matter.

Surface treatments are generally oxidative in nature and provide functional groups on the fiber surface which increase wettability and/or bondability. However, extensive oxidation can result in etching and severely reduce the carbon fiber strength which is very sensitive to surface flaws. Some work[86,87] was done to optimize the surface treatment process to increase interfacial shear strength without fiber property reduction.

It should also be noted that heat cleaning of graphite yarns, say at around 1000 °C in an inert nitrogen or argon atmosphere, is a desirable step before coating with a polymer surface film to improve adhesion.

A three stage mechanism was suggested to explain the oxidation of graphite in liquid medium[88]. Rodriguez et al.[88] observed a slower oxidation rate for natural than for synthetic graphite. A slower rate can be explained if the larger layers and their more perfect arrangement in natural graphite are taken into account.

The plasma is created by introducing the desired process gas into a vacuum chamber. The gas is excited by the application of radio frequency(RF) energy which dissociates the gas into electrons, ions, free radicals and metastable products. Electrons and free radicals created in the plasma collide with the polymer surface rupturing covalent bonds therefore creating free radicals on the polymer surface. Free radicals in the plasma may then combine with the polymer free radicals to provide thermodynamically preferred products.

The free radicals created by the plasma process have four main effects on polymers[89]:

- i) surface cleaning: plasma cleaning usually related to the removal of unbound organics from the surface. Cleaning is also effective in the removal of mold release or low molecular weight components in the formulation which can bloom to the surface.
- ii) ablation, a form of dry micro-etching: In this process it is the polymer substrate which is removed. Thus, plasma

is effective at removing the weak boundary layer that occurs during polymer processing. Amorphous polymer is removed many time faster than either crystalline polymer or inorganic material. This change in surface area can improve mechanical linkage and will increase the area available for chemical interactions.

iii) crosslinking and

iv) surface activation: The most dramatic and wide used effect of plasma treatment is in the surface modification of polymers, where the outside layers of polymeric material are altered to creat chemical groups and interactions of interest. Typically, this is done with the addition of polar functional groups which dramatically increase the surface energy of most polymers.

III. EXPERIMENTAL MATERIALS AND PROCEDURES

1. Materials

1). Epoxy Resin and Curing Agent

A diglycidyl ether of bisphenol A resin (DER 332) from the Dow Chemical Company was used in this experiment. DER 332 is a highly purified diglycidyl ether of bisphenol A with an average molecular weight of about 340-355, a viscosity of about 4000-6400 centipoises at 25 °C and a specific gravity of 1.16[4].

DER 332 was cured with aliphatic polyethertriamine (Jeffamine T-403) from Texaco Chemical Company with a specific gravity of 0.9812 and a viscosity of 76.5 centipoise at 25 °C. The epoxide and amine equivalent weights determined by chemical titration were 175.15 and 82.92g, respectively[5]. The resin-curing agent ratio used is the stoichiometric ratio of 47 amine parts per hundred epoxide parts (phr) T-403.

All materials were used as received without any purification. The structures of these materials are presented in Table 1.

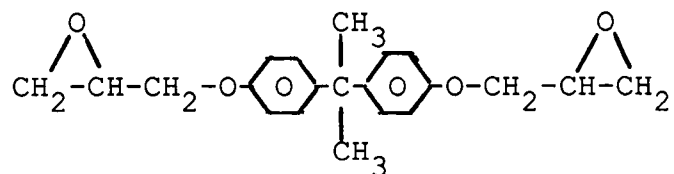
2). Graphite Fibers

In order to study the influence of the constituent materials on the mechanical properties and on the overall

Table 1. Chemical Structures of Materials

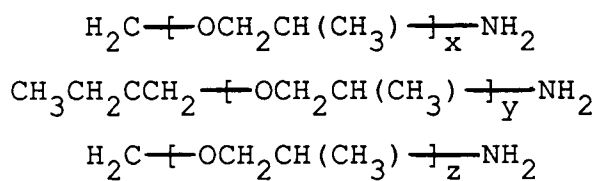
DER 332

:



Diglycidyl ether of bisphenol A

Jeffamine T-403 :



Polyether triamine

crack propagation behavior of the composites, three different types of graphite fibers were used. i) A pitch-based graphite fiber obtained from Union Carbide Corporation (Thornel Type p-55 grade VSB-16 with a density of 2.0g/cm^3), ii) a high modulus, relatively low strength, PAN-based graphite fiber obtained from Hercules Corporation (MagnaMite HMS with a density of 1.83g/cm^3) and iii) a low modulus, high strength, PAN-based graphite fiber (MagnaMite AS4 with a density of 1.80g/cm^3) were used to reinforce the epoxy matrix.

2. Sample Preparation

1) Plasma Etching

The Plasma-Prep II manufactured by SPI Supplies uses a radio frequency (RF) discharge. The operation of the Plasma-Prep II consists of loading the graphite fibers in the sample chamber, evacuating the sample chamber by using a vacuum pump, applying the oxygen into the sample chamber at a pressure of 5 psig, and applying the energizing RF power. The radio frequency is tuned to the lowest point on the meter (13.56 MHz). The graphite fibers are etched.

2) Preparation of Epoxy and Composite Samples

The fibers were wound uniaxially around the base of an

aluminum mold sprayed with a release agent (Kantstik 325). In order to measure the volume fraction of fiber, the total weight of fiber was measured. An aluminum frame was screwed on to the base of the mold and the mold was kept in an oven at 70 °C. The amounts of epoxy and curing agent were calculated with a stoichiometric ratio (47 phr T-403) and the amounts were controlled according to the volume fraction (10 - 45 % of fiber) approximately.

The DER 332 was then heated to 70 °C and mixed with the curing agent thoroughly with a glass stirring rod while being maintained at 70 °C. The epoxy was poured over the fibers. The mixture was degassed for 1 hour in a vacuum chamber, and then pressure was applied to the cover of mold to control the volume fraction by squeezing out the epoxy resin and to get uniform sample thickness. The epoxy sheets and composites were cured at room temperature for 24 h, post-cured at 85 °C for 16 h, slowly cooled (about -4 °C/min) to room temperature and then demolded.

The sheets were cut using a band saw. Before making testing specimens, the weight of sheet used was measured and then the weight of graphite fiber and epoxy were calculated. The procedure of calculation for volume fractions of fiber is described in appendix A. Unidirectional composites were made from each type of graphite fiber with epoxy used as the matrix. The volume fraction of fiber in the composite was

designed at the 10, 20, 30, 40, and 50 vol. % resin. The dimensions of the specimens are shown in Figure 1.

It is pointed out by the SEM results that the fibers could not be evenly distributed at the volume fractions used. Therefore, the volume fraction of fibers merely represent an average value.

3. Sample Characterization and Experimental Procedures

1) Density and Volume Fraction Measurement

The density of the matrix is measured in a density gradient column made of sodium bromide-water solution in the range of 1.130 to 1.275 g/cm³ at 25 °C. The density gradient column is constructed according to ASTM D 1505-68[91].

The apparent volume fraction of fibers in composites is

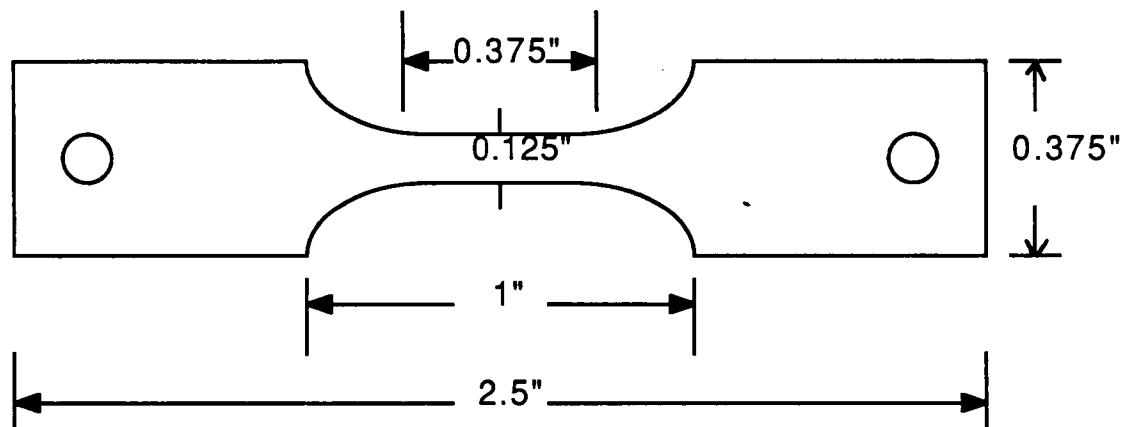
$$V_f = \frac{V_f}{V_f + V_m} = \frac{W_f/\rho_f}{W_f/\rho_f + W_m/\rho_m}$$

Where V_m is the volume fraction of matrix; ρ_f and ρ_m are the density of the fiber and matrix, respectively; W_f and W_m are the weight of the fiber and matrix, respectively.

2) Mechanical Test

Tensile strength, Young's modulus as well as interlaminar shear strength(ILSS) of the unidirectional

a. For Tensile Test



b. For 4 Point Bending Test

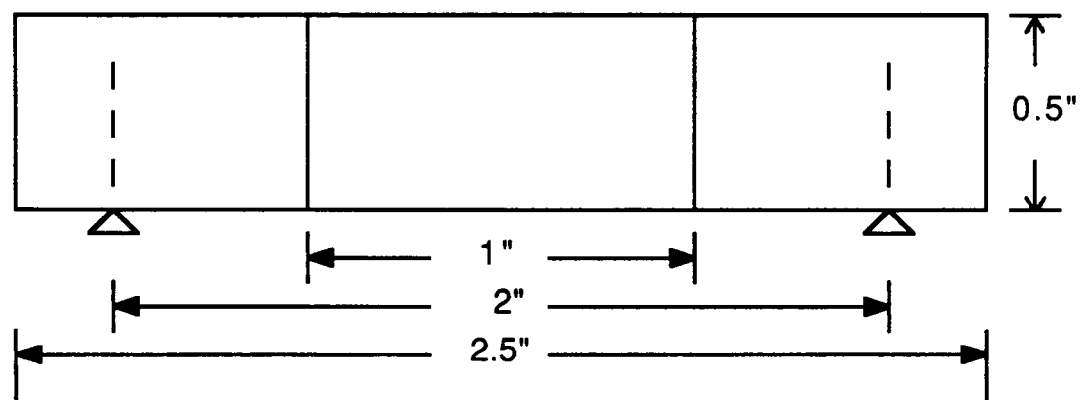


Figure 1. The dimensions of the specimens

graphite-epoxy composites were performed with the Instron Tester. Dogbone-shaped tensile specimens and specimens for shear testing were prepared from epoxy and composites. For epoxies, five tensile bars per sample were tested using an Instron Tensile Tester at room temperature. For composites, dogbone-shaped samples with four different volume fractions of fiber were made and tested using the Instron.

Tensile testing and shear testing were conducted in accordance with ASTM D 638-84[92] and ASTM D 2344-84[57], respectively.

The stress-strain curves were used to evaluate Young's modulus, tensile strength and interlaminar shear strength. The tensile strength at break is calculated from the equation

$$\sigma = F/A_0$$

where F is the force at break,

A_0 is initial cross sectional area.

The ultimate % elongation of the sample is determined from the equation

$$\% El = \epsilon \times 100 = 100 \times \frac{(\text{Cross head speed}) (\text{Chart distance})}{L_0 \times (\text{Chart speed})}$$

where ϵ is the strain,

L_0 is the initial gauge length of the specimen.

Young's modulus is calculated by the equation

$$E = \sigma/\epsilon$$

and is calculated from the initial slope of the stress-strain curve. Actually the Young's modulus is the secant modulus which corresponds to 0.5 % strain for fiber/epoxy composites and 1 % strain for epoxy resin. The samples were tested using a cross-head speed of 0.2 in/min.

ILSS is calculated as follows:

$$S_H = 0.75 P/bh$$

where S_H is interlaminar shear strength, P is breaking load, b is specimen width and h is specimen thickness. The samples were tested with cross-head speed of 0.1 in/min.

Every data point represents the average of four to five specimens.

3) SEM

An ARM model 900 high resolution scanning electron microscope was used to study the effect of plasma etching on graphite fibers and on the fracture surfaces of the composites. After mechanical testing, specimens were sectioned and prepared for microscopic analysis. A gold coating was deposited on the surfaces of sectioned specimens before SEM inspection to prevent static charging of the surface by the electron beam.

IV. RESULTS AND DISCUSSION

1. Mechanical Test

1) Four-Point Shear Test

The interlaminar shear mechanical behavior along the fiber axis direction of uniaxial graphite fiber reinforced epoxy with various fiber volume fractions and several etching conditions has been studied to investigate the effect of gas plasma etched graphite fiber on the ILSS of the composites.

The test results for the shear tests performed in this study are summarized in Table 2, 3, and 4. Data are shown for the PAN(poly acrylonitrile) based AS4 and HMS fibers and melt-spun pitch-based VSB-16 fibers reinforced epoxy as a function of fiber volume fractions and fiber etching times. The fiber volume fractions and etching time dependence of the composite failure is illustrated in Figures 2 to 7.

As shown in Table 2-4 and figure 2-4, the results of four-point bending tests showed that the ILSS of composites did not change greatly with etching time. However, recent studies[82] using plasma revealed that ILSS was increased with fiber surface treatment. From the SEM studies, the fibers showed almost no change in fiber surface with 2 min and 4 min plasma etching. These results explain well why the ILSS of composites did not increase greatly with etching

Table 2. ILSS of AS4

Sample	Average ILSS	Volume Fraction
Condition	(MPa)	(%)
No etching	12.4	18
	14.1	20
	15.2	21
	15.9	22
	17.3	25
	20.4	27
	16.9	33
	8.9	38
	7.4	42
	7.1	43
2 min etching	12.8	11
	14.7	15
	11.9	30
	10.4	39
	9.2	43
4 min etching	9.3	15
	10.3	16
	10.4	18
	12.3	22
	15.9	25
	15.3	28
	10.7	46

Table 3. ILSS of HMS

Sample	Average ILSS	Volume Fraction
Condition	(MPa)	(%)
No etching	11.4	15
	11.5	18
	11.6	20
	12.2	26
	13.7	33
	12.9	38
	12.2	40
	11.8	42
2 min etching	11.9	18
	12.9	20
	13.6	24
	13.2	25
	14.1	32
	12.1	38
	10.7	45
4 min etching	11	15
	11	20
	12.2	23
	14	29
	11.4	40

Table 4. ILSS of VSB-16

Sample	Average ILSS	Volume Fraction
condition	(MPa)	(%)
No etching	5.3	14
	6.6	17
	7.3	22
	7.9	22
	7.1	31
	6.2	35
	6.5	41
2 min etching	6.9	17
	7.7	19
	7.6	25
	6.7	29
	6.3	30
4 min etching	6.8	17
	7.1	21
	6.6	22
	5.7	26
	5.4	39

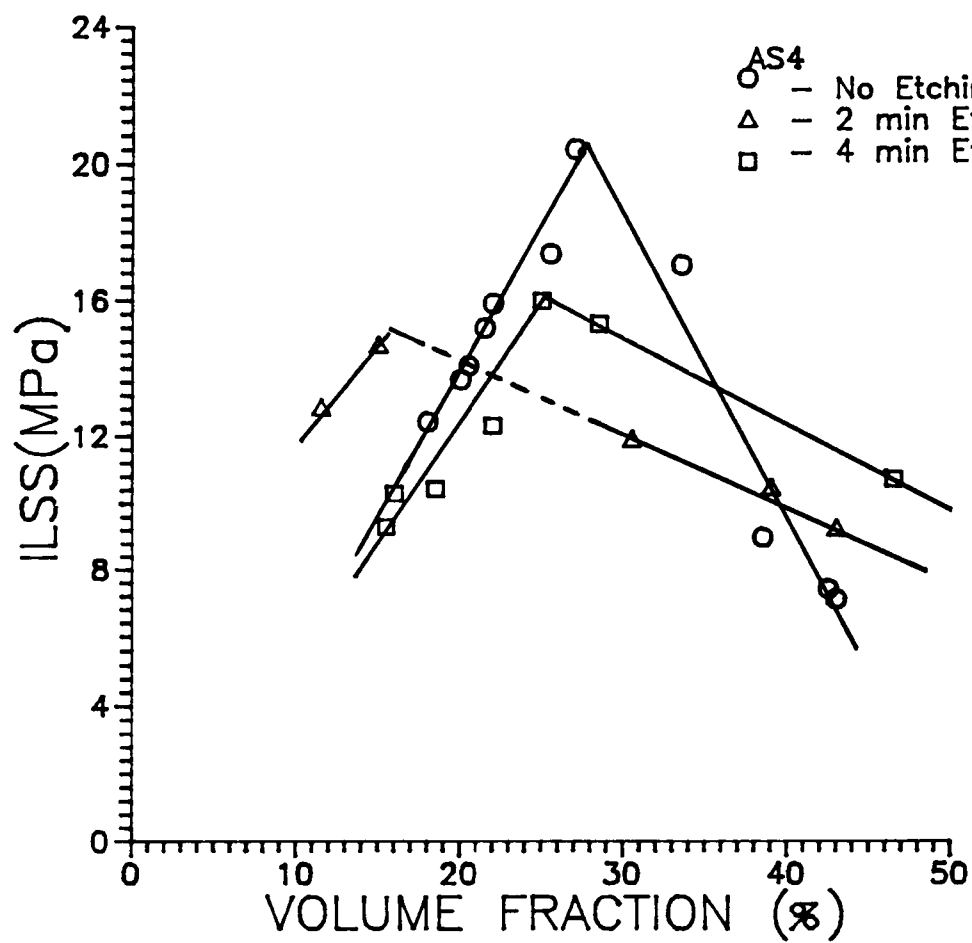


Figure 2. ILSS of AS4/epoxy composites.

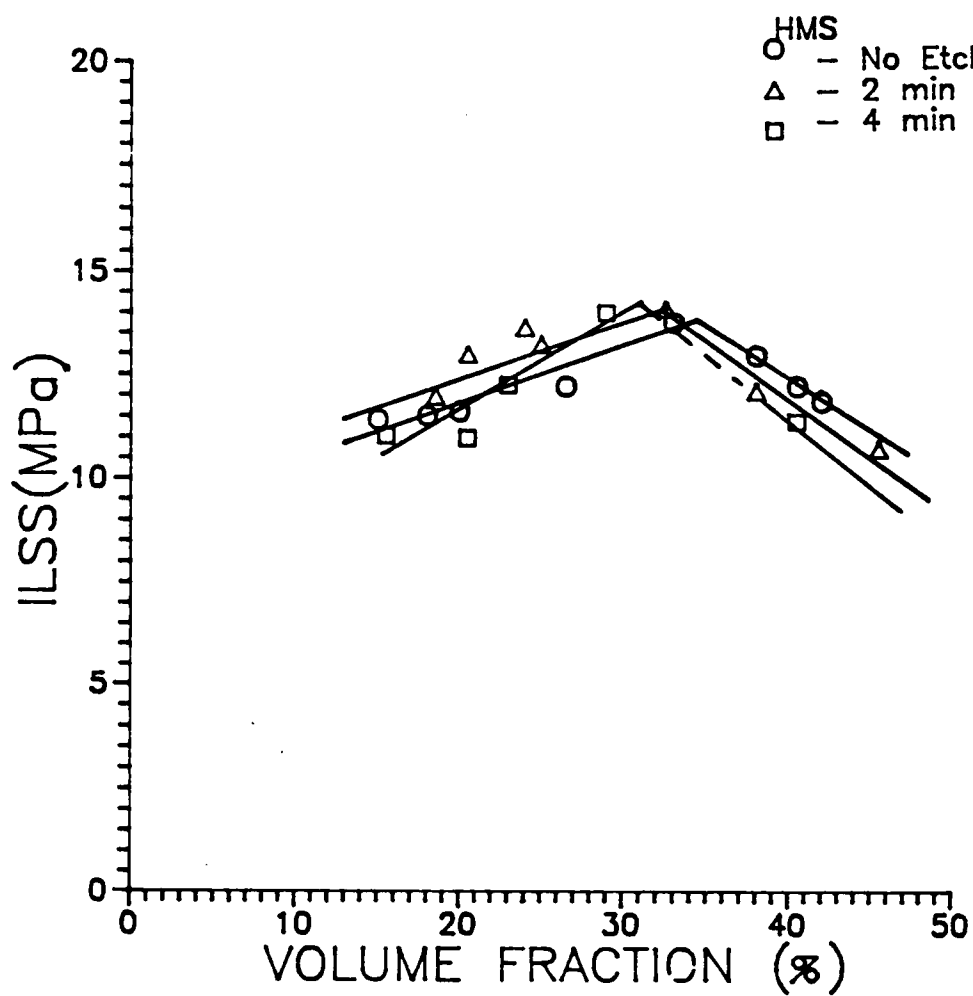


Figure 3. ILSS of HMS/epoxy composites.

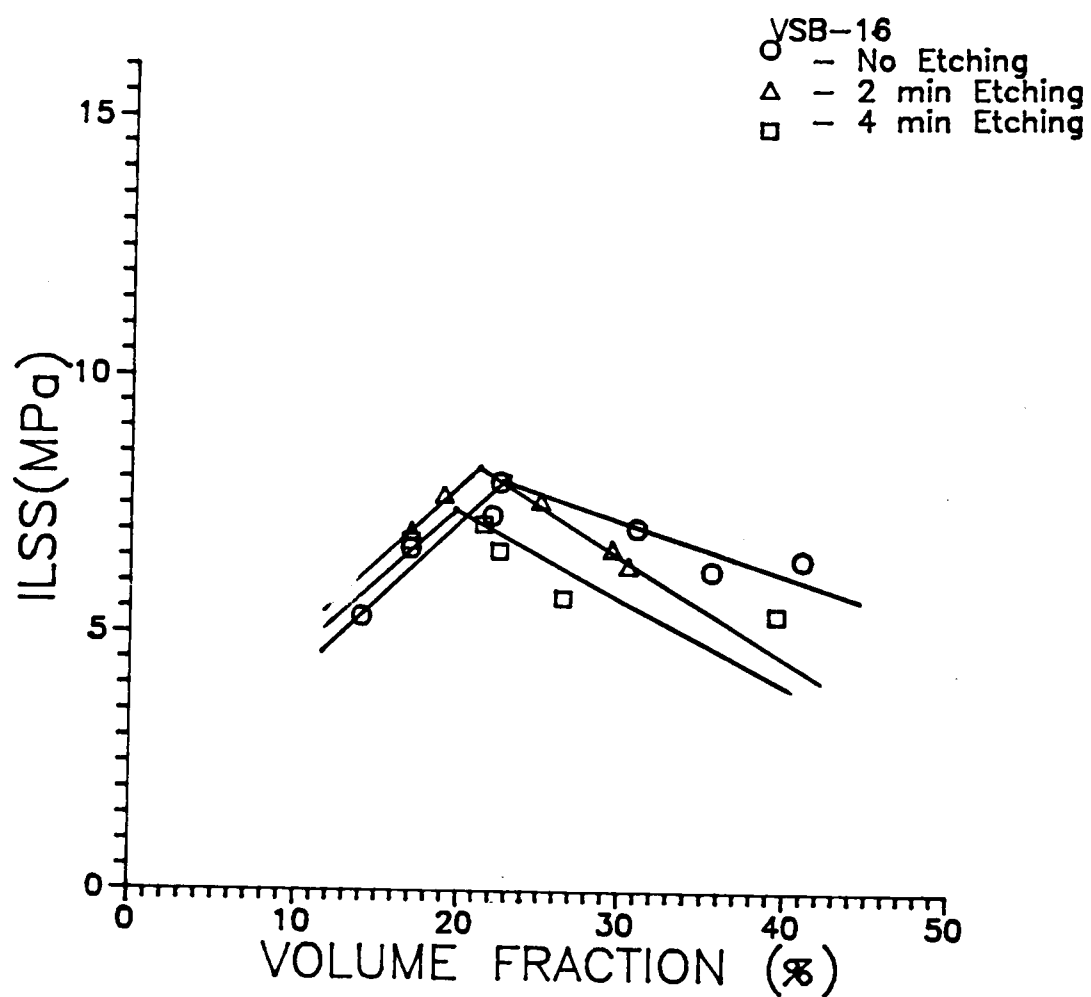


Figure 4. ILSS of VSB-16/epoxy composites.

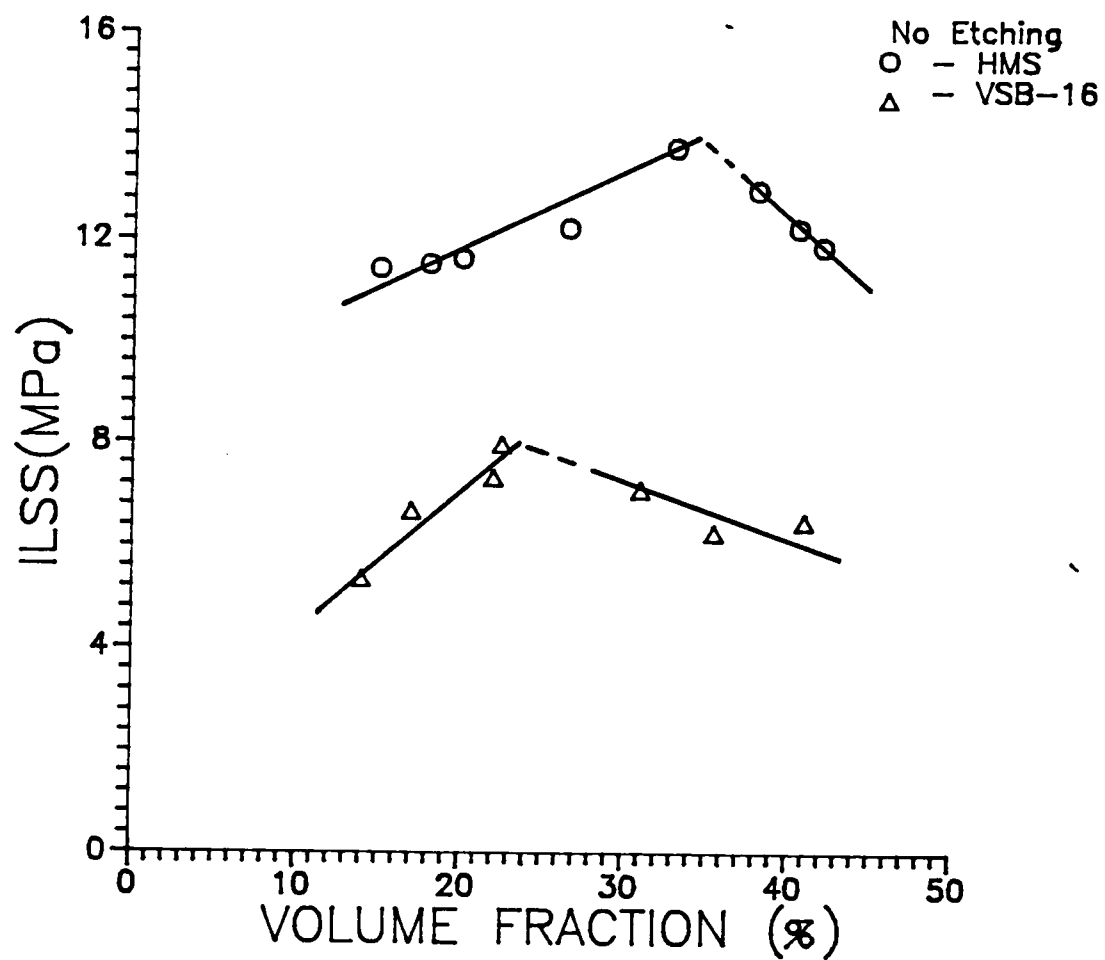


Figure 5. Comparison of ILSS at no etching.

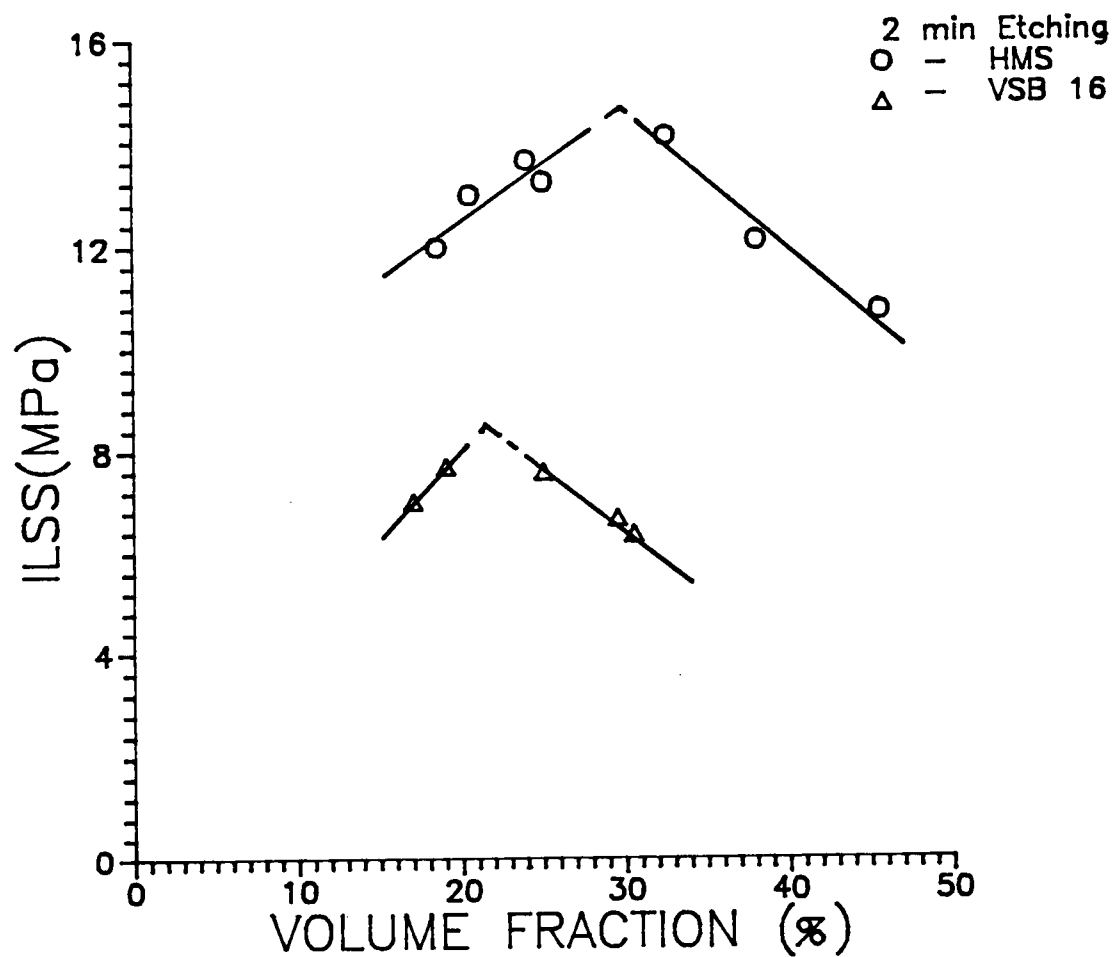


Figure 6. Comparison of ILSS at 2 min etching.

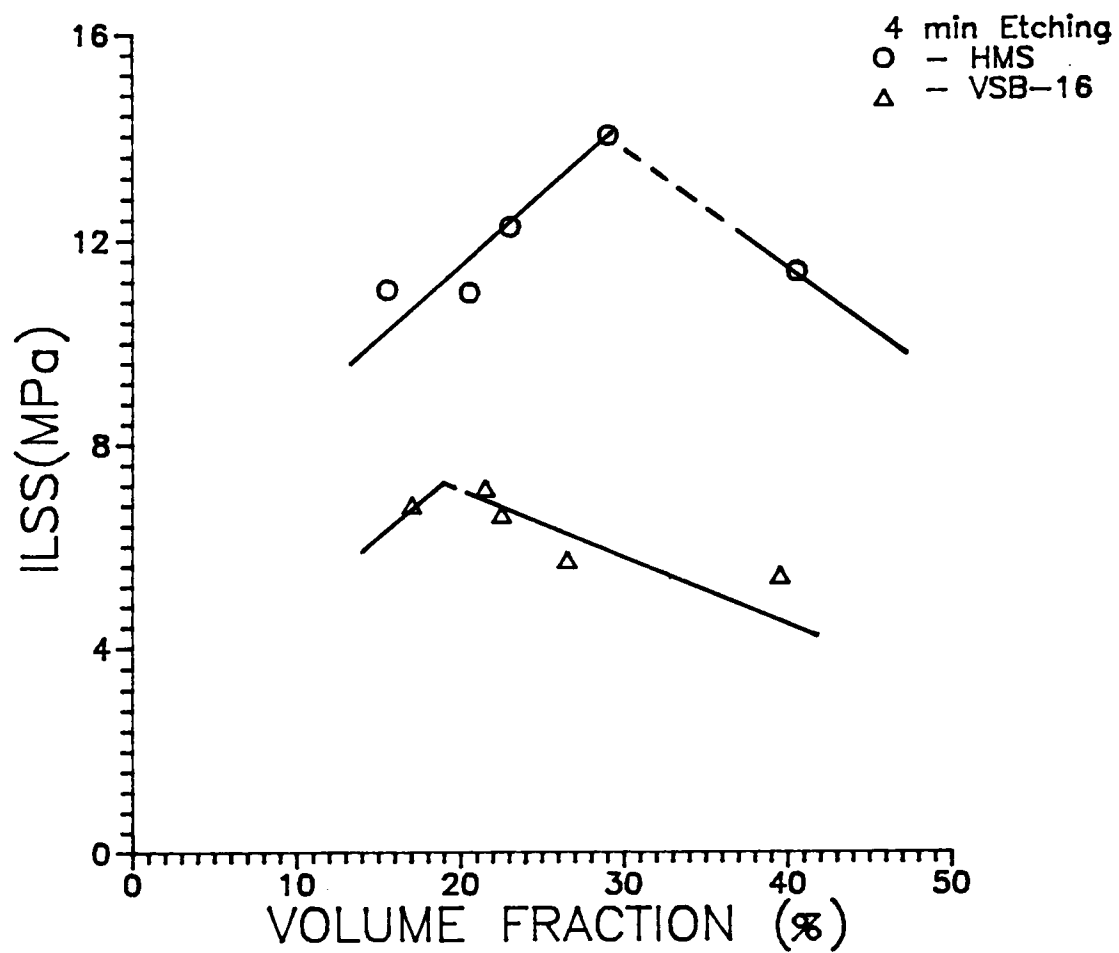


Figure 7. Comparison of ILSS at 4 min etching.

time. Novak[43] observed that ILSS of as-received graphite/epoxy composites decreased but ILSS of surface treated fiber/epoxy composites was increased as fiber volume fraction (about 25 % to 70 %) was increased. In these studies, the ILSS of composites at all etching conditions changed with fiber volume fractions and showed maximum points at about 20-25 %, 30 %, and 20 % fiber volume fraction for AS4/epoxy, HMS/epoxy, and VSB-16/epoxy respectively. This existence of the maximum values for the ILSS in the range of the fiber volume fractions from 20 % to 30 % indicates that there exists optimum fiber volume fraction for the reinforcing effectiveness to improve the ILSS. Many people[62,79,84] used 55-65 % fiber volume fraction in measuring the ILSS. It suggests that they found the maximum and/or optimum ILSS at 55-65 % fiber volume fraction. In these studies, samples with a maximum 45 % fiber volume fraction could be made. Thus, the optimum fiber volume fractions showing maximum ILSS are much lower than those of other papers. Below the fiber volume fraction showing the maximum ILSS, the ILSS of composites made from 2 min etching fibers was greater than that of composites made from no etching fibers and the ILSS of 4 min-etching-AS4-fibers/epoxy was smaller than that of no etching-AS4-fibers/epoxy composites suggesting that the AS4 fibers were degraded by 4 min etching. As shown in figures 5, 6, and 7,

the PAN-based AS4 and HMS fibers/epoxy composites showed the greater ILSS than the pitch-based VSB-16 fibers/epoxy[35].

2) Tensile Test

The tensile properties of unidirectional graphite fiber/epoxy resin composites with various fiber volume fractions have been studied to investigate the influence of the constituent material on the mechanical properties using a Tensile Tester.

The test results for the tensile tests are summarized in Table 5. The stress-strain curves are shown in Figure 8 to 12. As shown in the stress-strain curves and Figures 13 and 14, the tensile strengths and moduli of the AS4/epoxy, HMS/epoxy, and VSB-16/epoxy composites increased as the volume fraction of fibers increased. AS4/epoxy composites showed greater tensile strengths but lower moduli than HMS/epoxy composites.

Two cases of failure mode were observed in this study; i) ductile plastic deformation by the PAN-based AS4/epoxy composites, ii) brittle catastrophic failure shown by the pitch-based VSB-16/epoxy composites. A maximum of 15 % tensile strain of DGEBA-T403 epoxies[5] was attained for the highest crosslinked glass, showing much higher percent elongation comparing with the result of my studies. However, it was known that the cure temperature[85] affected

Table 5. The Tensile Test

Sample	Tensile	% Elongation	Modulus	Volume
	Strength(MPa)	(%)	(GPa)	Fraction(%)
AS4	405	8.7	11.5	13
	531	9.2	12.6	16
	700	8.3	19.4	21
			19.7	19
			22.8	25
			26.3	28
HMS	149	2.6	13.3	9
	279	4.3	18.3	13
	489	6.3	22.6	21
VSB-16	137	1.3	14.9	13
	137	1.6	15.2	15
	231	1.1	24.2	20
	286	1.2	30.9	27
Epoxy	73	5.3	3.9	
	66	5.9	3.3	
	70	6.4	3.4	

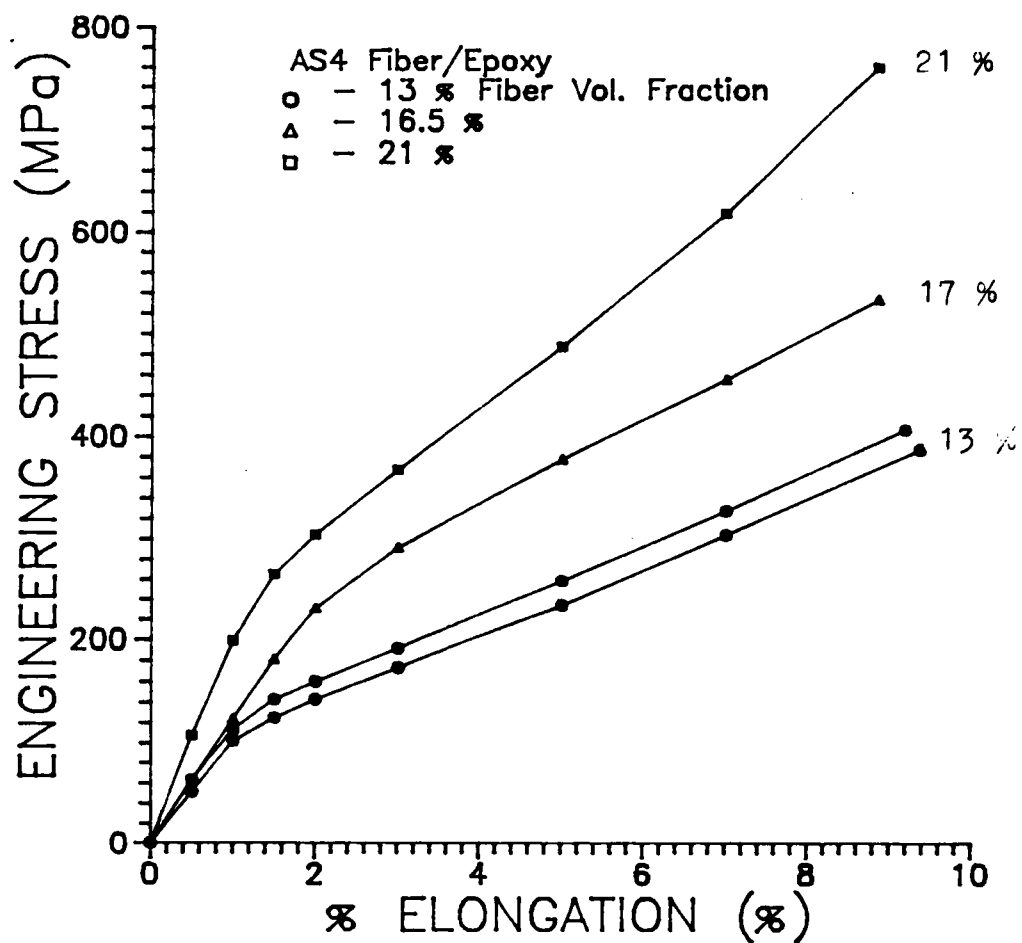


Figure 8. Stress-strain curves of AS4/epoxy composites.

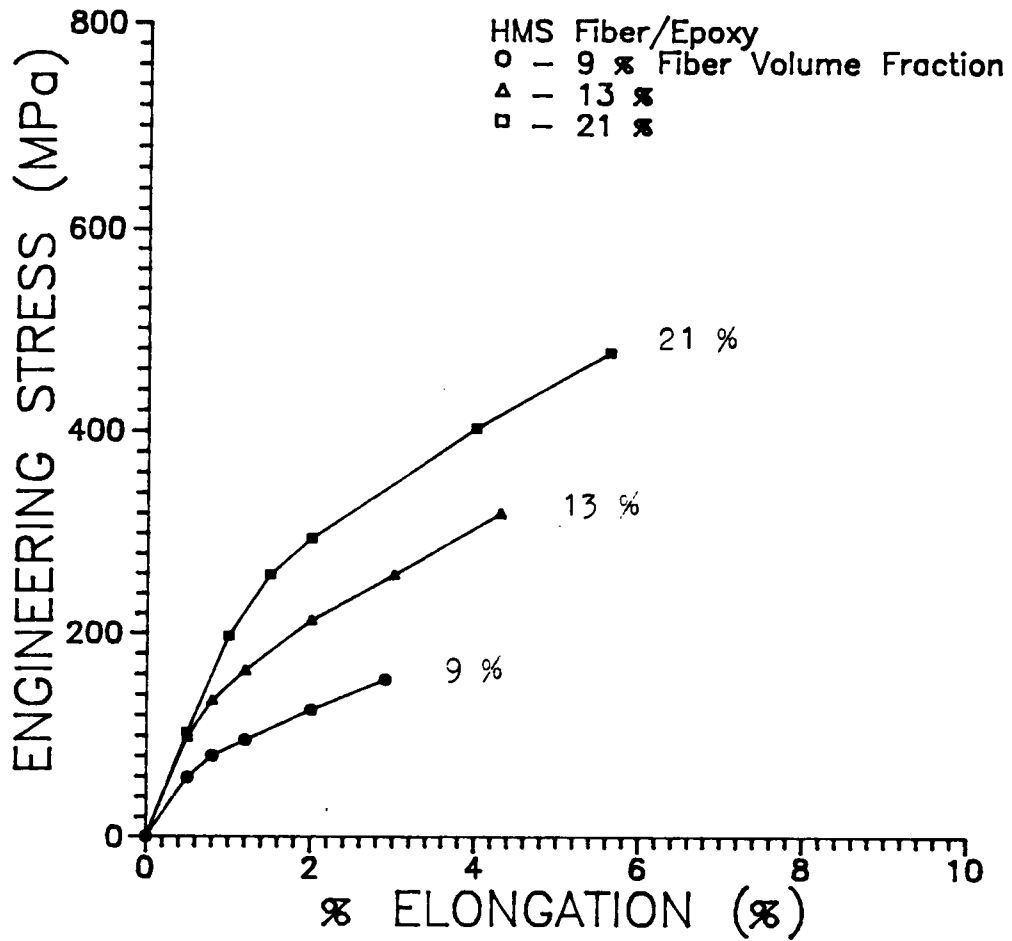


Figure 9. Stress-strain curves of HMS/epoxy composites.

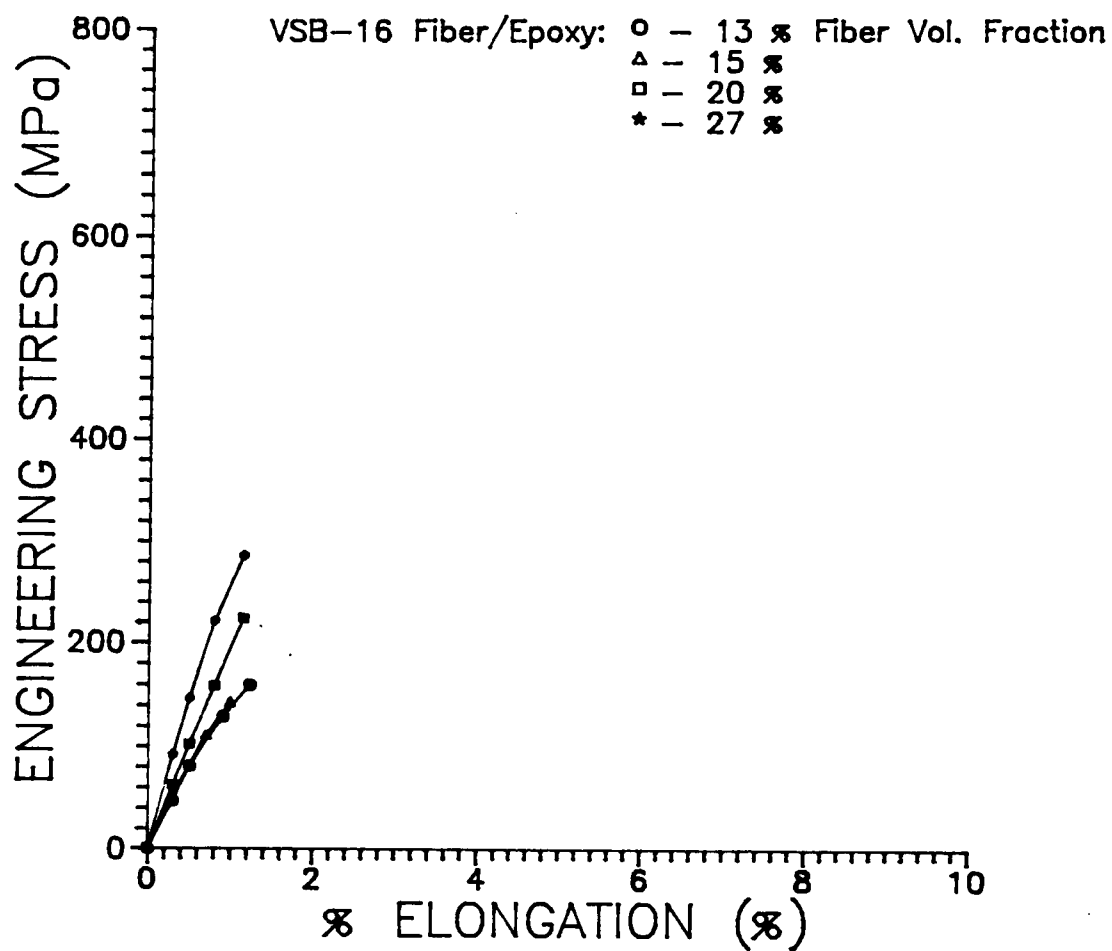


Figure 10. Stress-strain curves of VSB-16/epoxy composites.

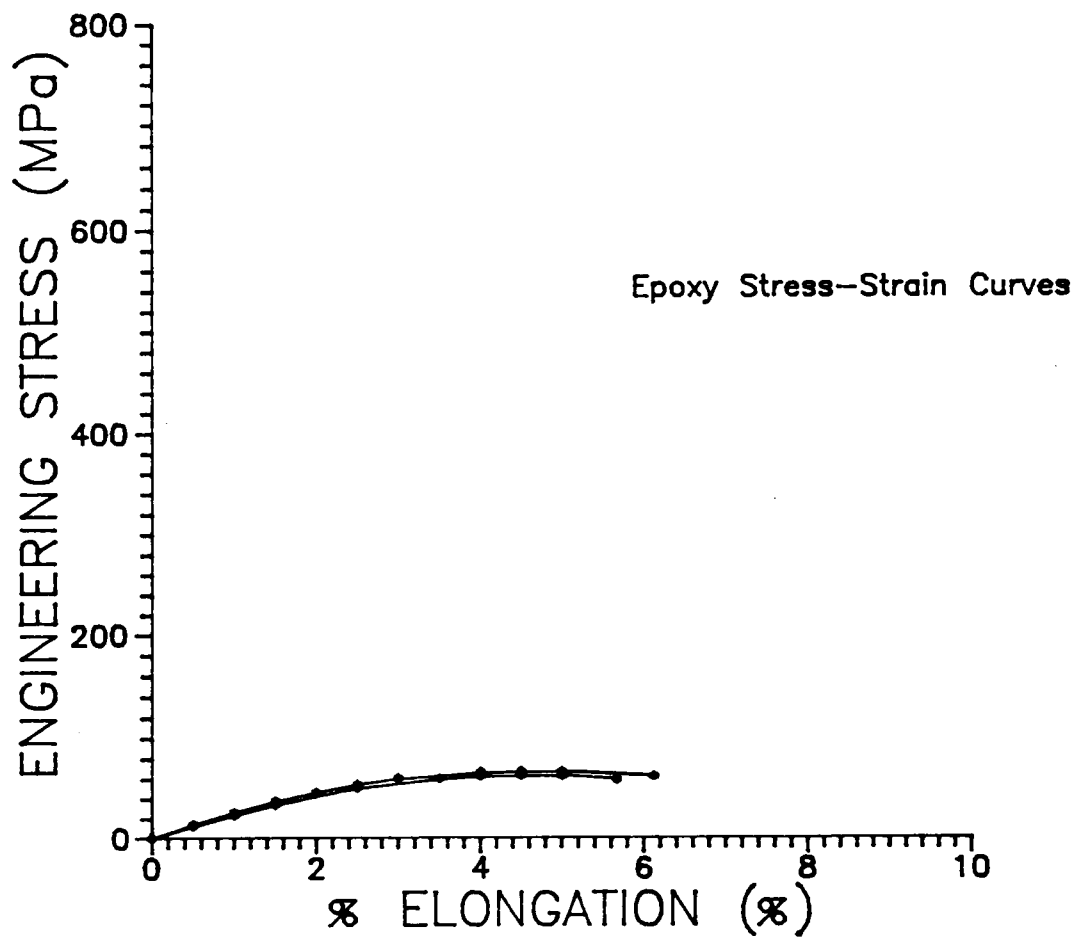


Figure 11. Stress-strain curves of epoxy.

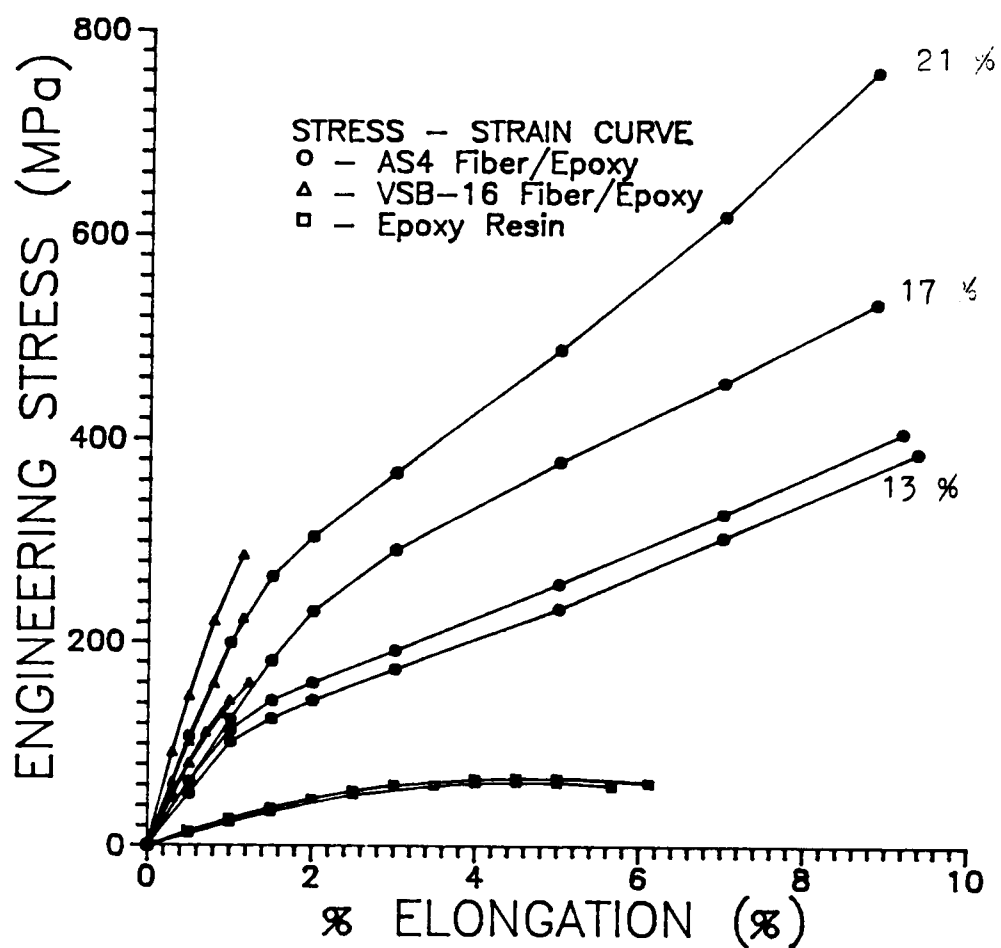


Figure 12. Comparison of stress-strain curves.

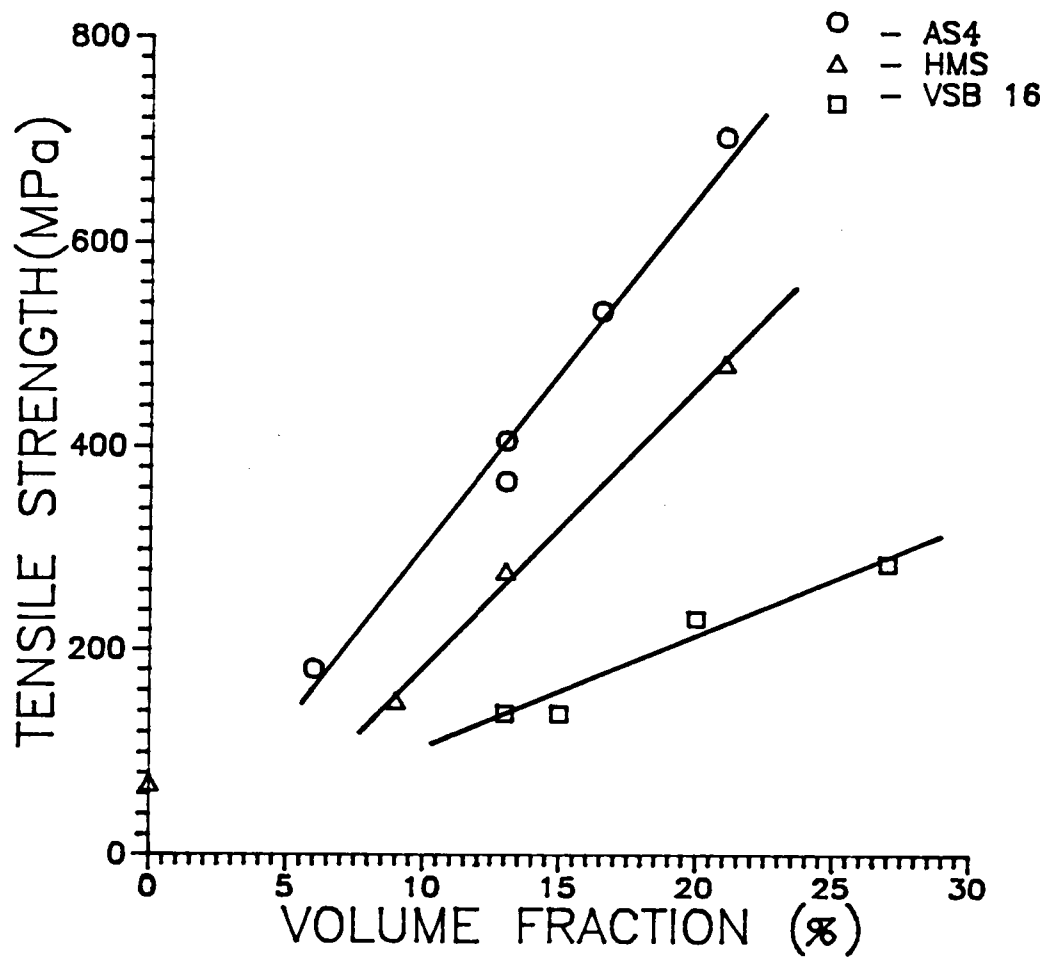


Figure 13. Tensile strength vs. volume fraction.

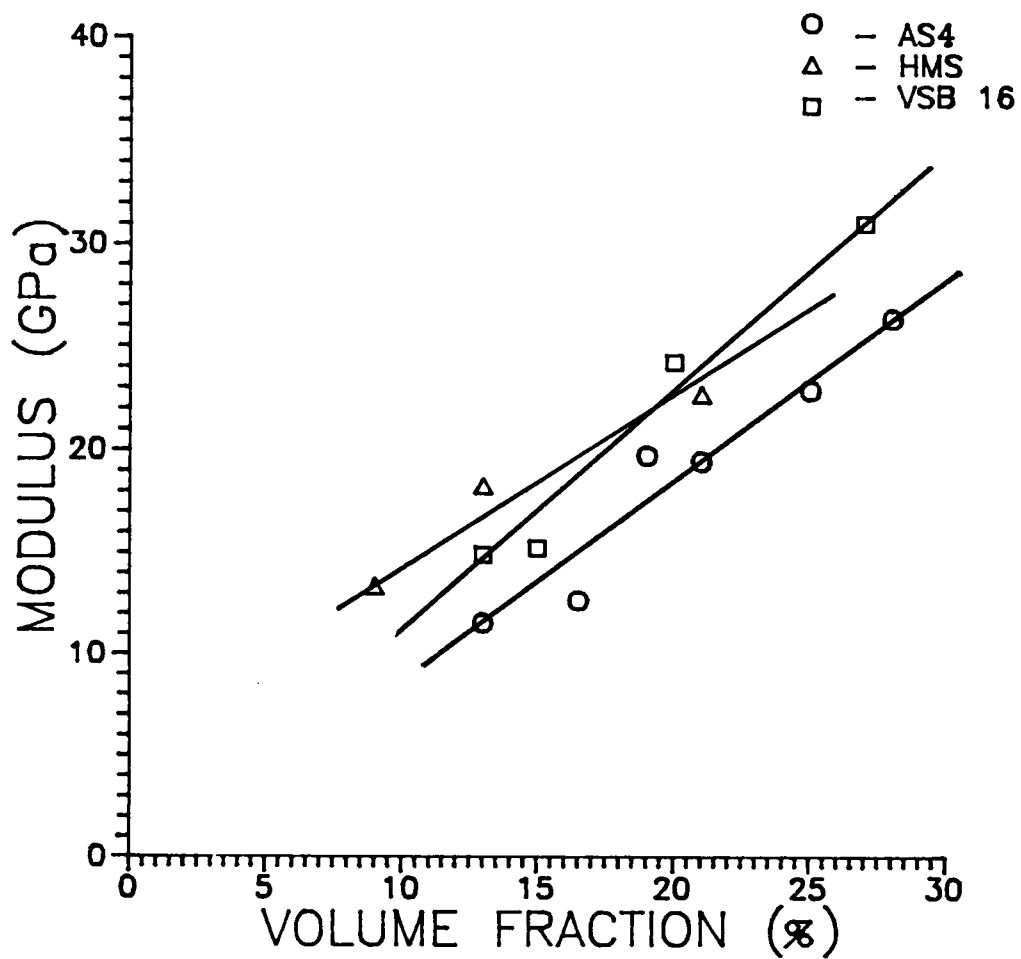


Figure 14. Modulus vs. volume fraction.

the mechanical properties of resins and cooling rate[64] played a particularly important role in determining the morphology of the reinforcement matrix boundary region. A different heating process was used, therefore, different percent elongation was measured. Particularly significant findings in this study are: i) the percent elongation of AS4/epoxy composites in the longitudinal direction is much higher than that of individual components, epoxy and fibers as shown in Figure 15. ii) the stress-strain curves of AS4 fiber/epoxy composites in Figure 8 show yielding and these composites deformed by ductile plastic manner. This yielding is not expected for a normally brittle and highly crosslinked epoxy/fiber composites. Yielding is mentioned in some papers[49,51,55,63]. However the results were obtained from bending tests and single filament tests, not from tensile tests. From this unique characteristic of the curves, the tensile curves of AS4/epoxy composites suggest: i) these composites are tough materials - high stress at break and high elongation. ii) fibers were broken and fibers/matrix debonding occurred at the yield stress.

The ductile deformation accompanied by the yielding is interpreted to result from shear stress concentration due to the fiber breakage, as a result of the shear stress, the matrix around the fiber broken tip yielded and plastic deformation was formed along the fiber sides. The ductile

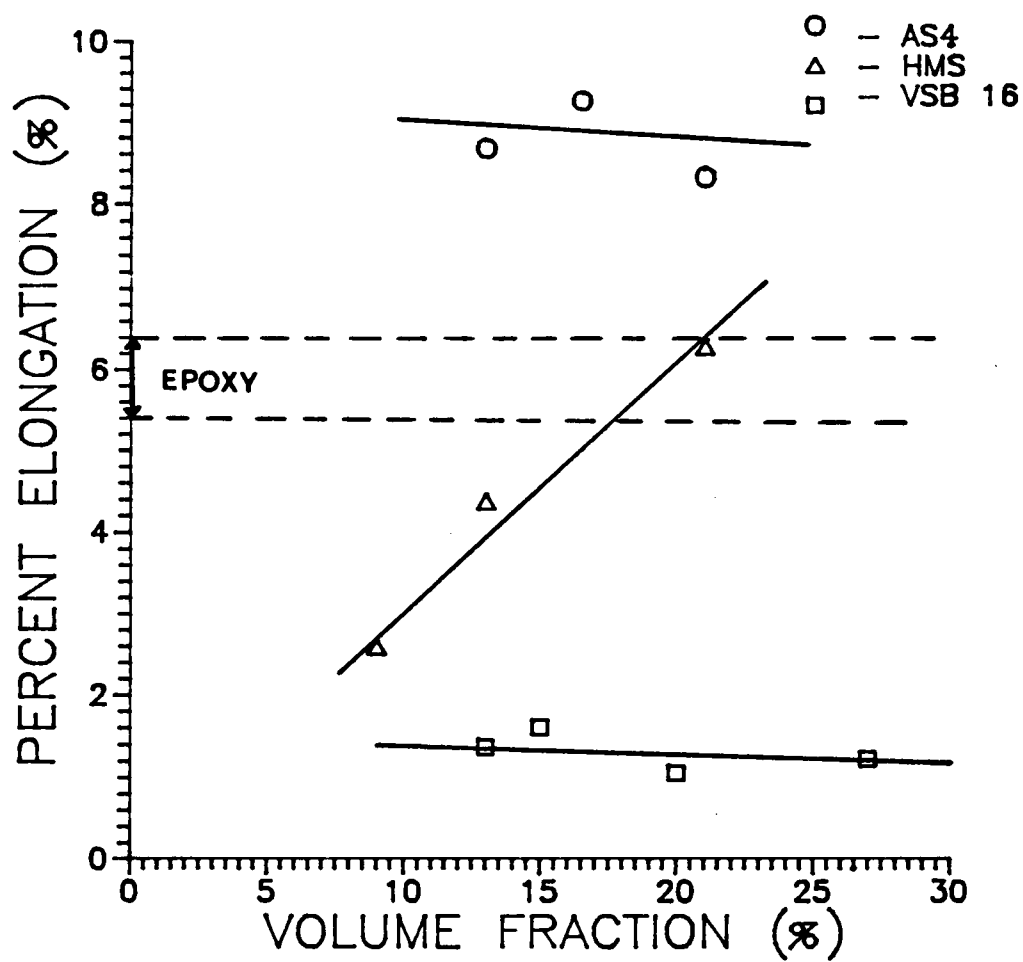


Figure 15. Percent elongation vs. volume fraction.

failure is considered to absorb the fracture energy of the fiber, suggesting that matrix deformation accompanied by fiber breakage is considered to contribute to the fracture toughness of the composites. Considerably different behavior occurred in the VSB-16 and HMS/epoxy composites. The percent elongation of VSB-16/epoxy composites was lower than that of individual components. The HMS/epoxy composites showed that the percent elongation increased from about the value of fiber % elongation to that of epoxy % elongation.

There are some direct correlations between results of 4-point bending tests and those of tensile tests. The higher the tensile strength, the higher the ILSS shown by AS4/epoxy composites. The higher the ILSS, the lower the modulus (AS4/epoxy). The lower the ILSS, the higher the modulus shown by VSB-16/epoxy. Thus, these results show that the ILSS of composites is strongly dependent on the fiber modulus.

The comparison of tensile strength data from tensile test with those from four-point bending test are summarized in Table 6 and shown in Figures 16, 17, and 18. As shown in Figures, the tensile strength data from tensile test is greater in AS4/epoxy composites, but lower in VSB-16/epoxy composites than those from four-point bending test. From Figure 17, the tensile strengths of HMS/epoxy composites

Table 6. Comparison the Tensile Strength from Tensile Test¹ and Four-Point Bending Test²

Sample	¹ Tensile	Volume	² Tensile	Volume
	Strength(MPa)	fr(%)	Strength(MPa)	fr(%)
AS4	405	13	407	18
	531	17	546	20
	700	21	562	20
			601	22
			754	27
			803	33
			616	42
HMS	149	9	357	15
	279	13	493	20
	489	21	808	33
			892	37
			842	40
			834	42
VSB-16	137	13	204	14
	137	15	309	17
	231	20	420	22
	285	27	488	22
			660	31
			599	35
			596	41

²Tensile strength from 4 point bending test[60].

$$\tau_{\max} = \sigma_{\max}/S$$

where, $\tau_{\max}$ = maximum interlamin shear
strength

$\sigma_{\max}$ = maximum tensile strength

$$S = L/h$$

L = length of specimens

h = thickness of specimen.

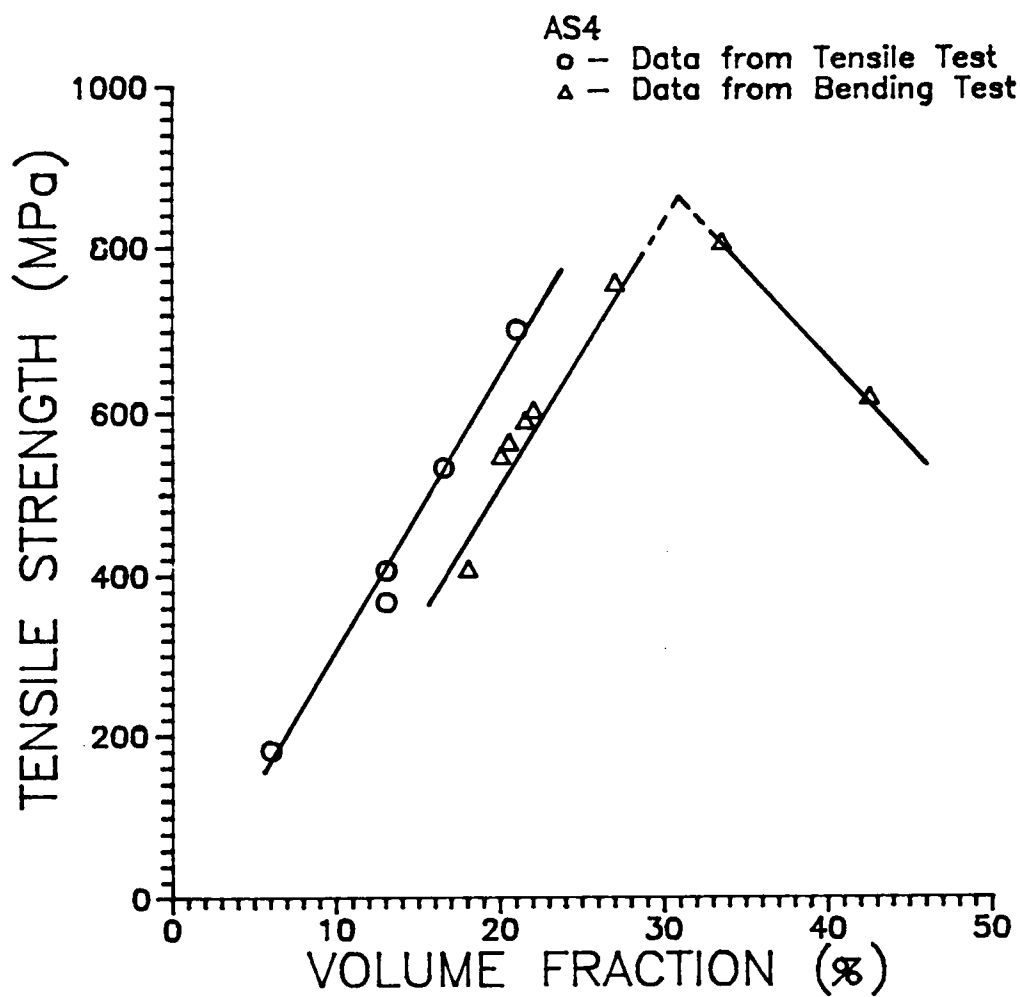


Figure 16. Comparison of AS4/epoxy tensile strength from tensile test and from bending test.

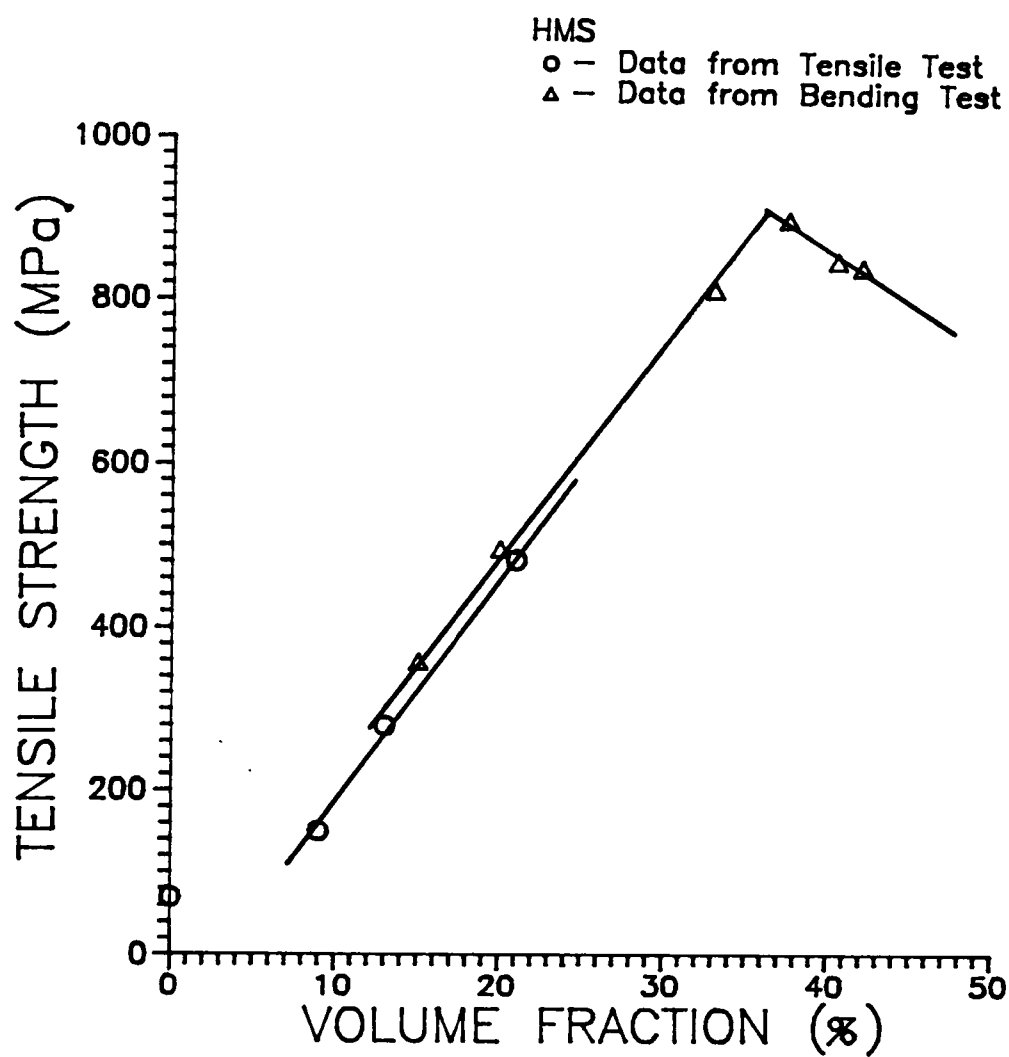


Figure 17. Comparison of HMS/epoxy tensile strength from tensile test and from bending test.

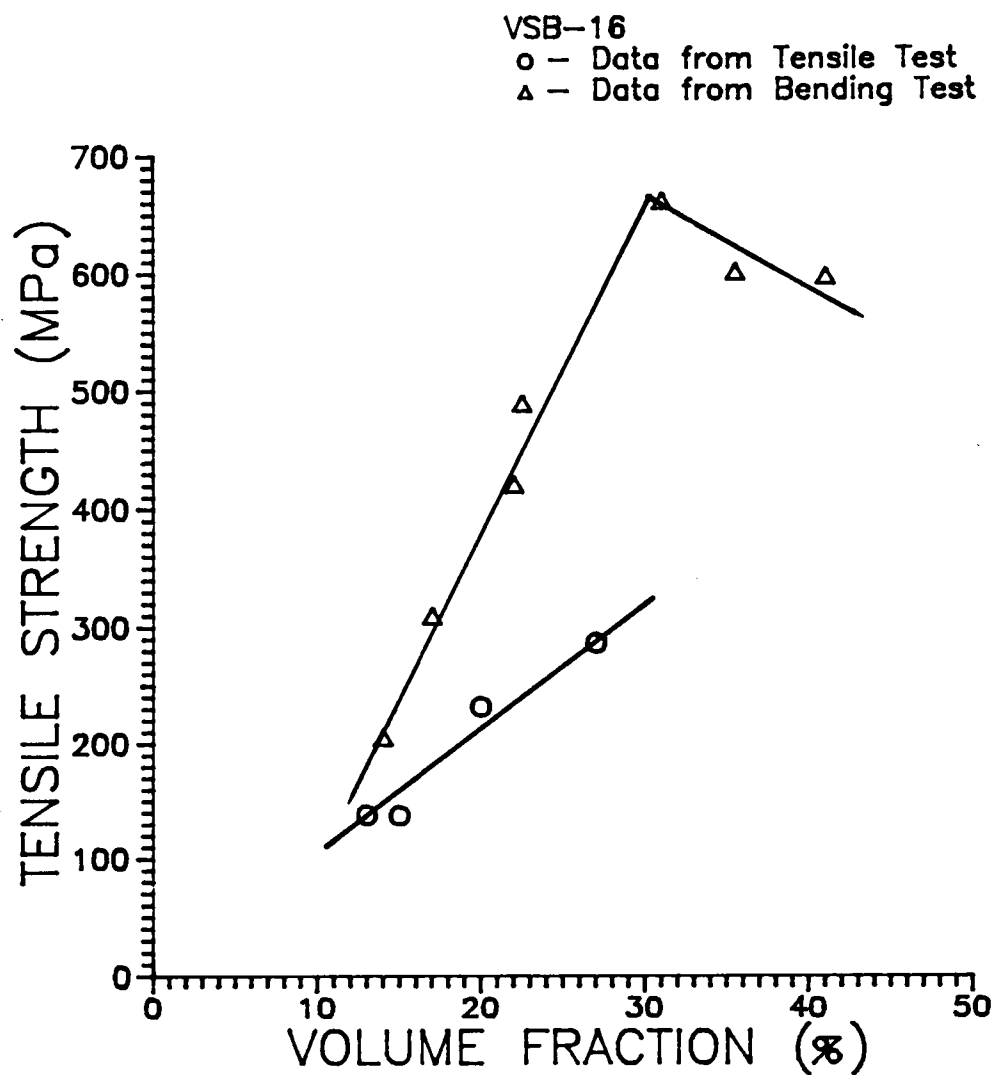


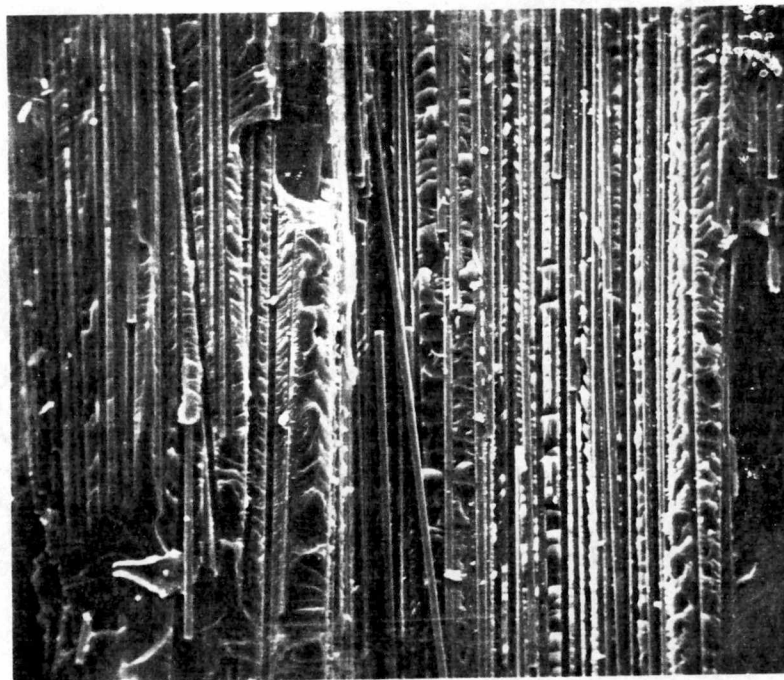
Figure 18. Comparison of VSB-16/epoxy tensile strength from tensile test and from bending test.

from both tests are almost the same below about 35% fiber volume fraction.

2. SEM Studies

The scanning electron micrographs of the unetched (2 min and 4 min) AS4 (HMS and VSB-16) fibers and fracture surfaces under tension (and under bending) were taken to correlate the results of mechanical tests with the fracture surface morphology.

The SEM micrographs of fibers showed almost no change in fiber surface with 2 min and 4 min plasma etching. One can imagine two reasons: i) the etching time was too short to etch the fibers. However, it was frequently observed during plasma etching processing that the plasma was strong enough to burn some parts of the fibers. ii) the etching was not done well because of instrument difficulties during the etching process. One of the most striking aspects of interlaminar shear failure surface of AS4/epoxy composites is the delamination as shown in Figures 19 - 21. Two dominant features on the delaminated surfaces were exposed graphite fibers and hackle formation in the matrix[56]. The hackles tend to slant in the same direction over the entire surface[56]. An arrow (-->) indicates the direction of crack propagation. The fracture surfaces of HMS/epoxy



(a)

Figure 19. The SEM of the fracture surface of
unetched AS4/epoxy composites - under bending

(a) 200x - 22% fiber volume fraction

(b) 500x - 18% fiber volume fraction

(c) 1000x - 27% fiber volume fraction

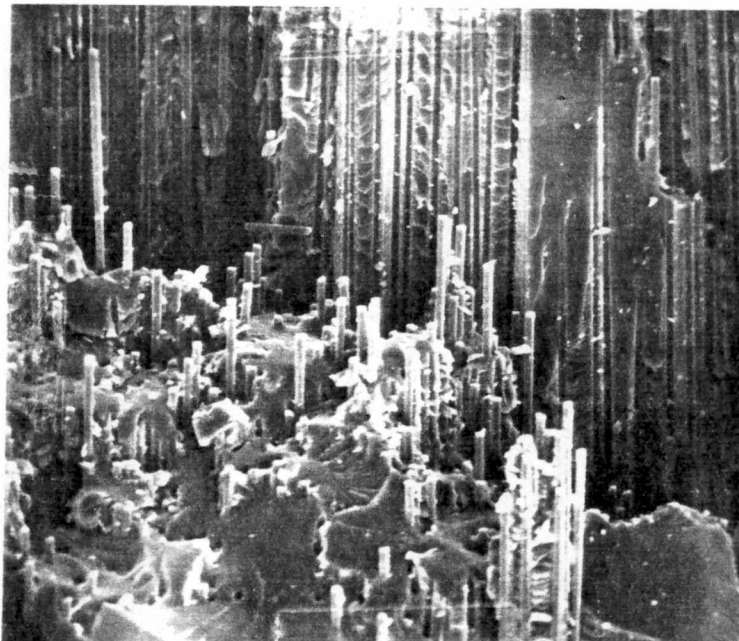


(b)



(c)

Figure 19 (continued)



(a)

Figure 20. The SEM of the fracture surface of 2 min etched AS4/epoxy composites-under bending

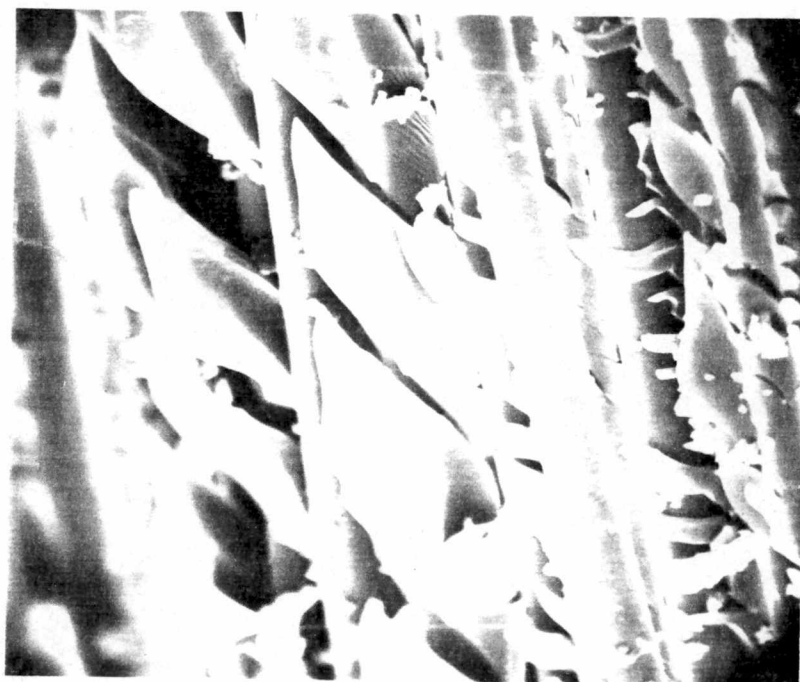
(a) 200x - 30.5% fiber volume fraction

(b) 500x - 15% fiber volume fraction

(c) 1000x - 12% fiber volume fraction



(b)



(c)

Figure 20 (continued)



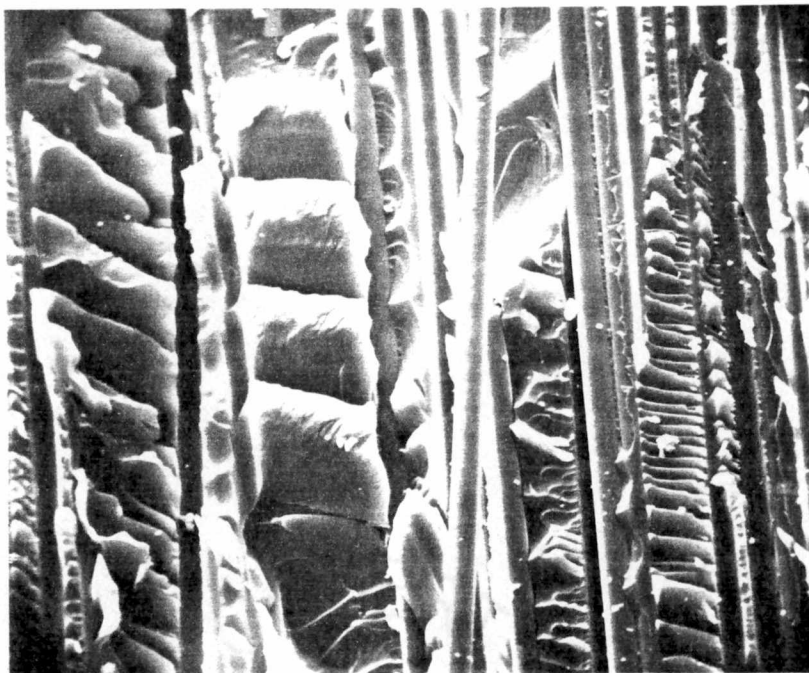
(a)

Figure 21. The SEM of the fracture surface of 4 min etched AS4/epoxy composites - under bending

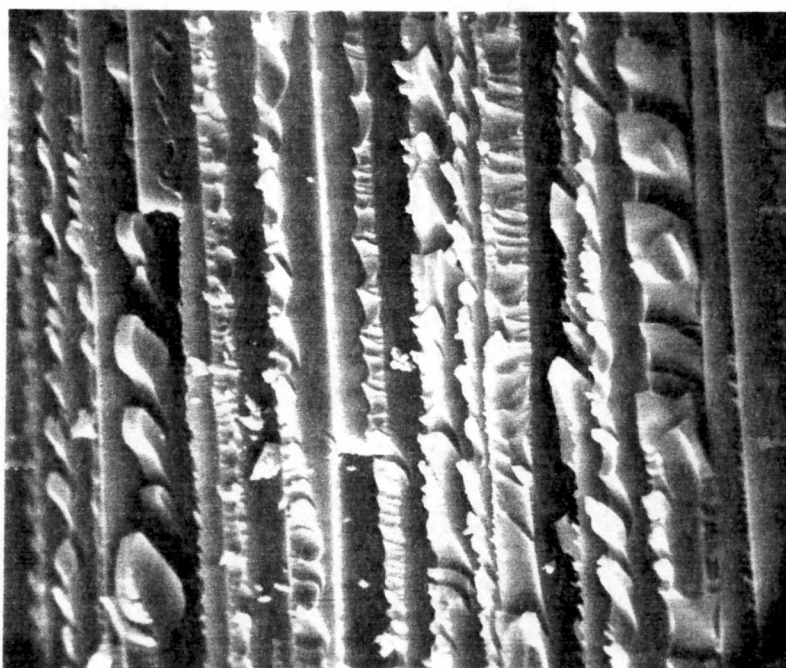
(a) 200x - 22% fiber volume fraction

(b) 500x - 15.5% fiber volume fraction

(c) 1000x - 28% fiber volume fraction



(b)

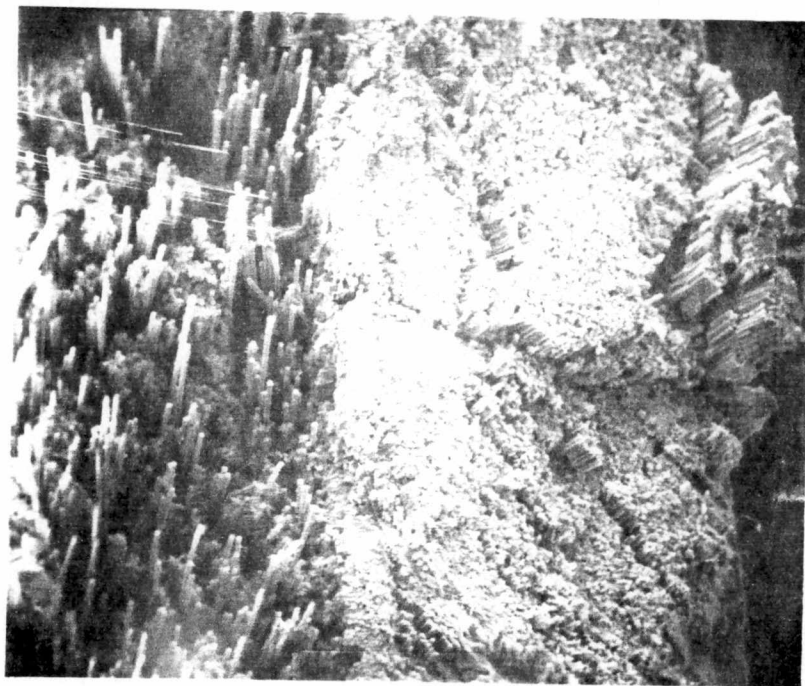


(c)

Figure 21 (continued)

composites are shown in Figures 22 - 24. HMS/epoxy composites under bending test showed tensile(compressive) failure as well as shear failure. As we can see in Figures 22-(a) and 23-(b), one side of the fracture surface shows a tensile failure and the other side shows a compressive failure. VSB-16/epoxy composites under bending test showed only tensile or compressive failure as shown in Figures 25 - 27. The fracture surfaces of bending test are almost the same as those of tensile test.

Figure 28(a) shows a general fracture surface of AS4/epoxy composites under tension. As shown in Figure 28(a-d), the principal fracture features were fiber pull-out (bundles and single fibers) and very rough fracture surface due to the pull-out of fiber bundles with epoxy. As fibers or fiber bundles are broken, a difference in the moduli develops between broken fibers (or bundles) and neighboring unbroken area. Since shear stresses are proportional to the difference of the moduli of the two phases, shear stress resulted from the interfaces of broken and unbroken fibers (or bundles) formed small hackles in the matrix as shown in Figure 28(d, e, and f). Figure 28(g and h) show the fiber surface roughening by the pull-out of fiber bundles with epoxy. The composites showing fiber pull-out (bundles and single fibers) with epoxy relax the stress concentration of the composites around the fiber effectively by the interface



(a)

Figure 22. The SEM of the fracture surface of unetched
HMS/epoxy composites - under bending

(a) 100x - 38% fiber volume fraction

(b) 500x - 18% fiber volume fraction

(c) 1000x - 26% fiber volume fraction

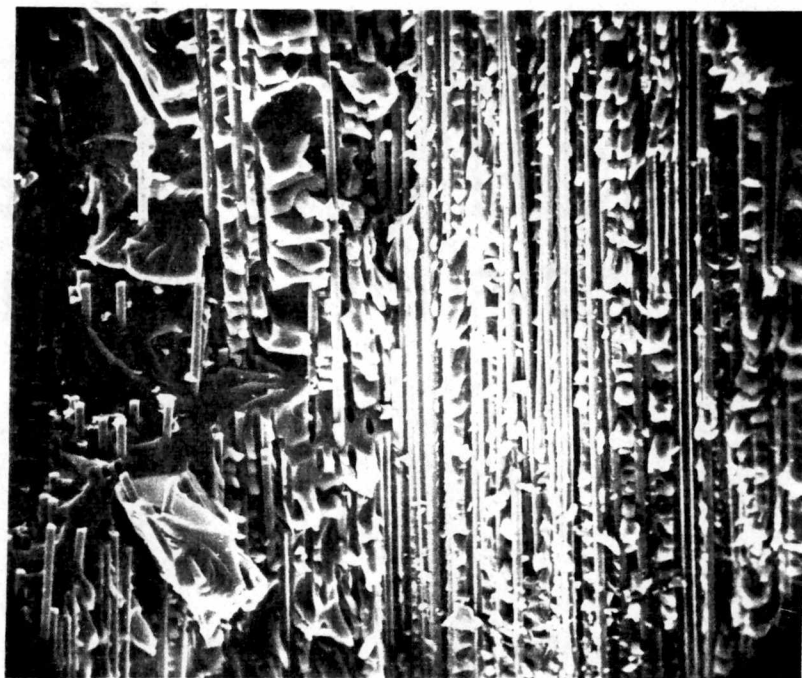


(b)



(c)

Figure 22 (continued)



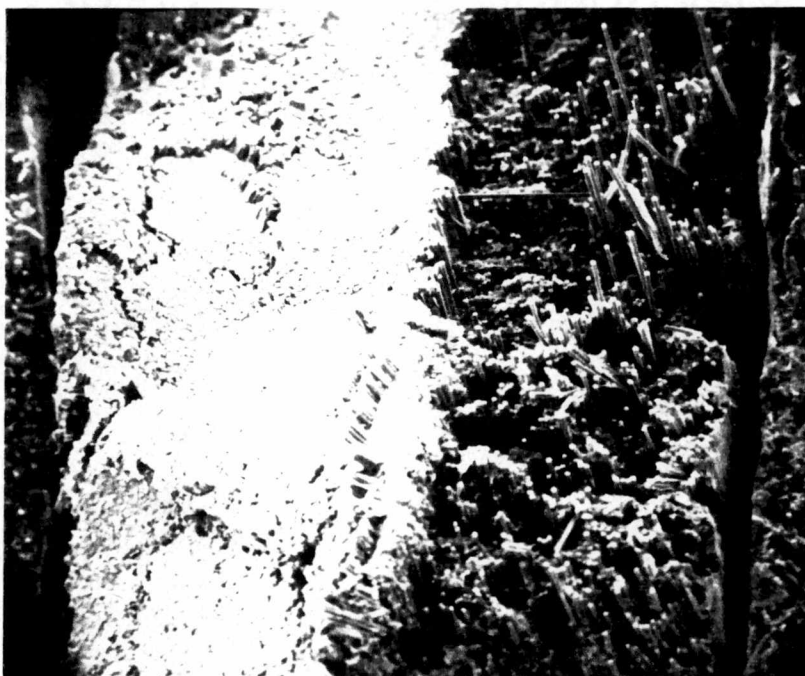
(a)

Figure 23. The SEM of the fracture surface of 2 min etched HMS/epoxy composites - under bending.

(a) 200x - 20.5% fiber volume fraction

(b) 100x - 32.5% fiber volume fraction

(c) 1000x - 32.5% fiber volume fraction



(b)



(c)

Figure 23 (continued)



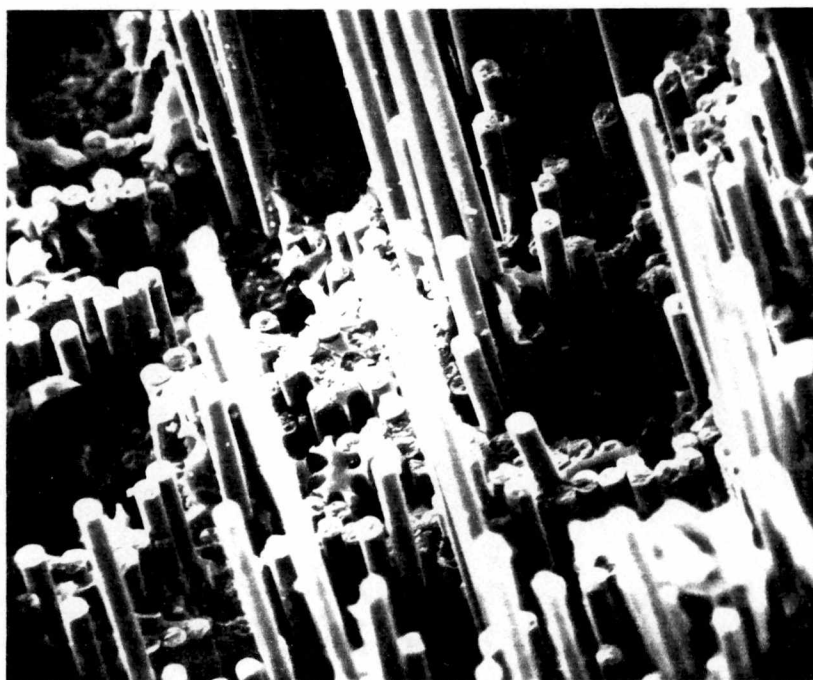
(a)

Figure 24. The SEM of the fracture surface of 4 min etched HMS/epoxy composites - under bending

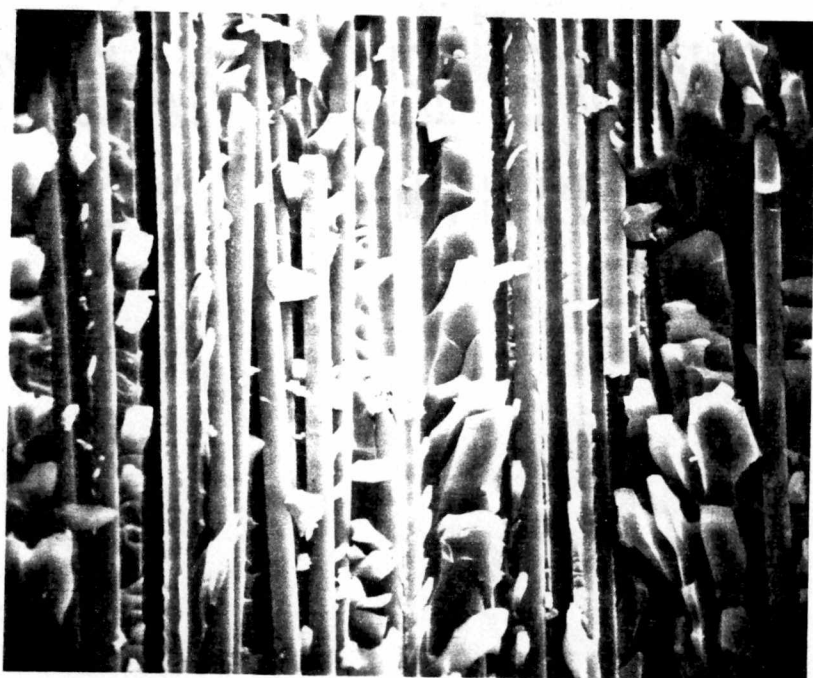
(a) 200x - 21% fiber volume fraction

(b) 500x - 29% fiber volume fraction

(c) 500x - 15.5% fiber volume fraction



(b)



(c)

Figure 24 (continued)



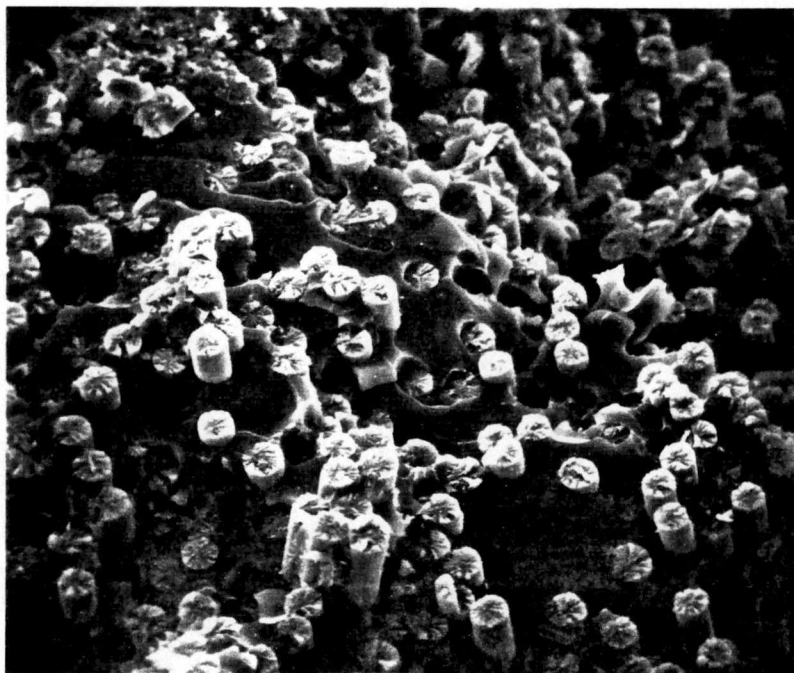
(a)

Figure 25. The SEM of the fracture surface of unetched VSB-16/epoxy composites - under bending

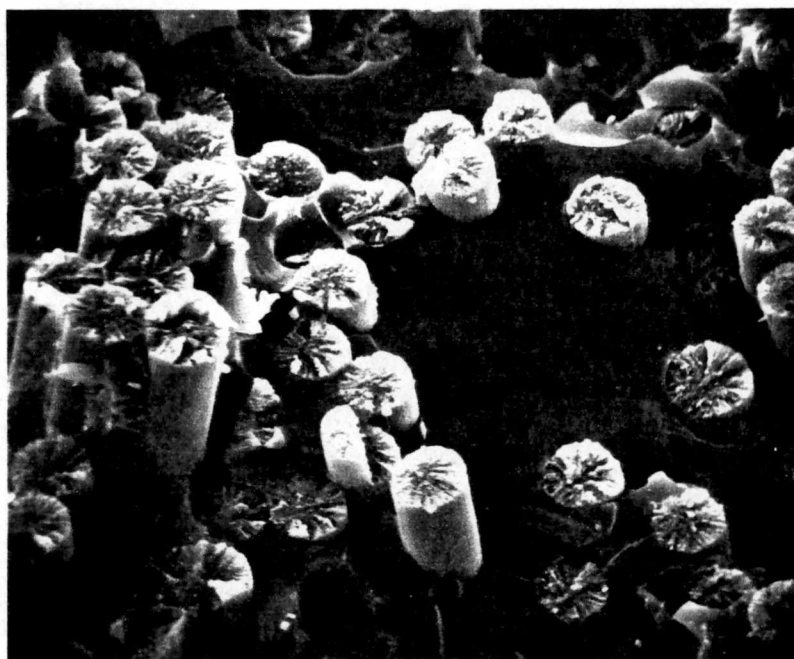
(a) 100x - 41% fiber volume fraction

(b) 500x - 31% fiber volume fraction

(c) 1000x - 22% fiber volume fraction

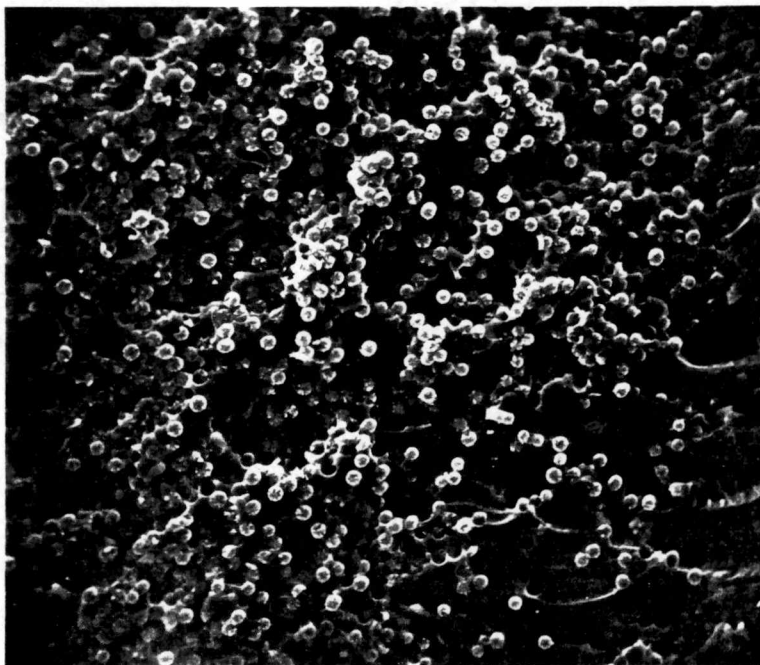


(b)



(c)

Figure 25 (continued)



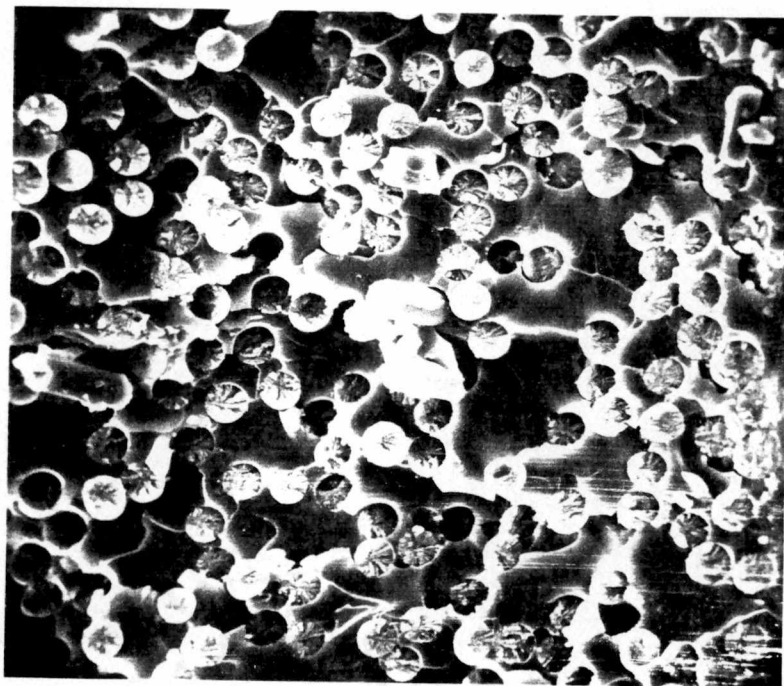
(a)

Figure 26. The SEM of the fracture surface of 2 min
etched VSB-16/epoxy composites - under bending

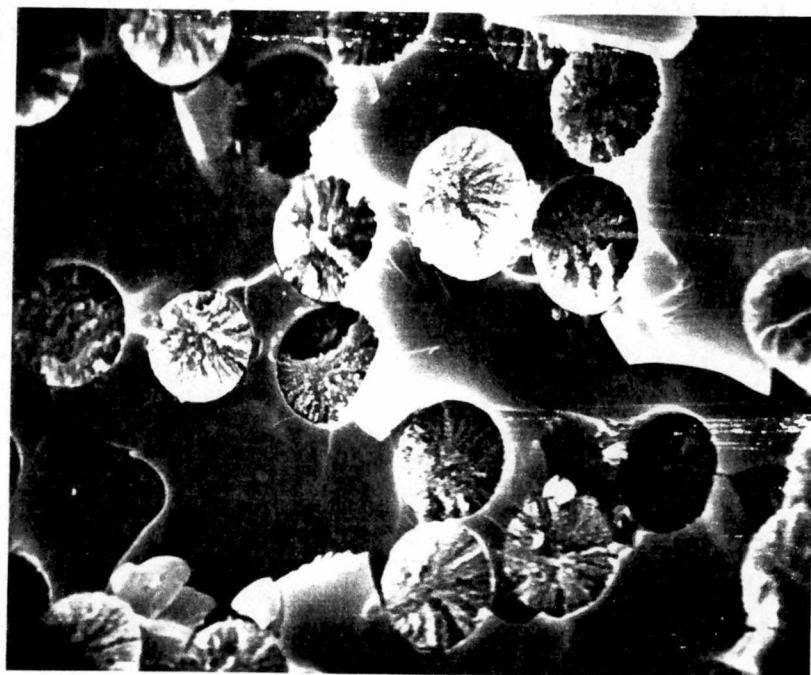
(a) 200x - 17% fiber volume fraction

(b) 500x - 30.5% fiber volume fraction

(c) 2000x - 25% fiber volume fraction

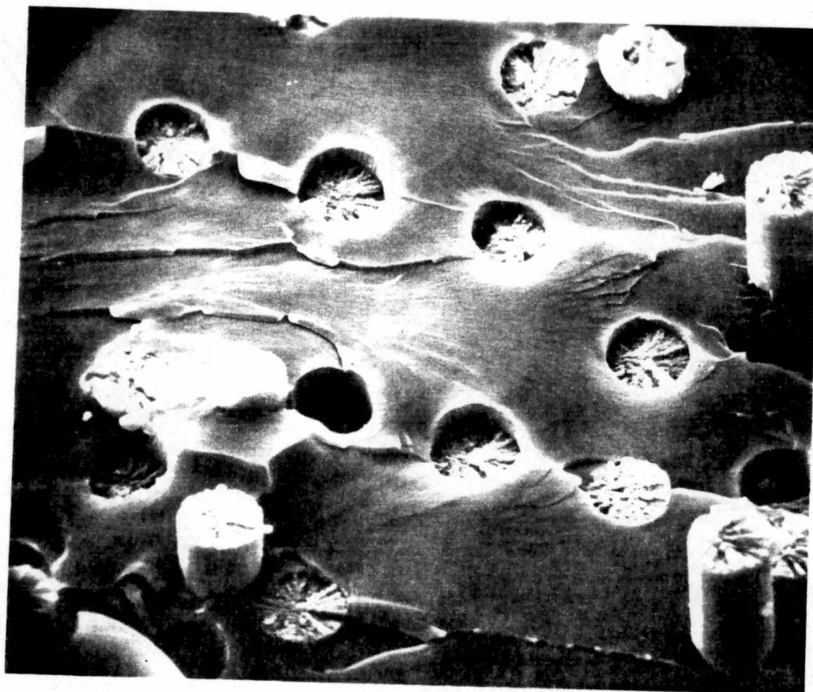


(b)



(c)

Figure 26 (continued)



(a)

Figure 27. The SEM of the fracture surface of 4 min etched VSB-16/epoxy composites - under bending

(a) 1000x - 17% fiber volume fraction

(b) 2000x - 21.5% fiber volume fraction

(c) 5000x - 26.5% fiber volume fraction



(b)

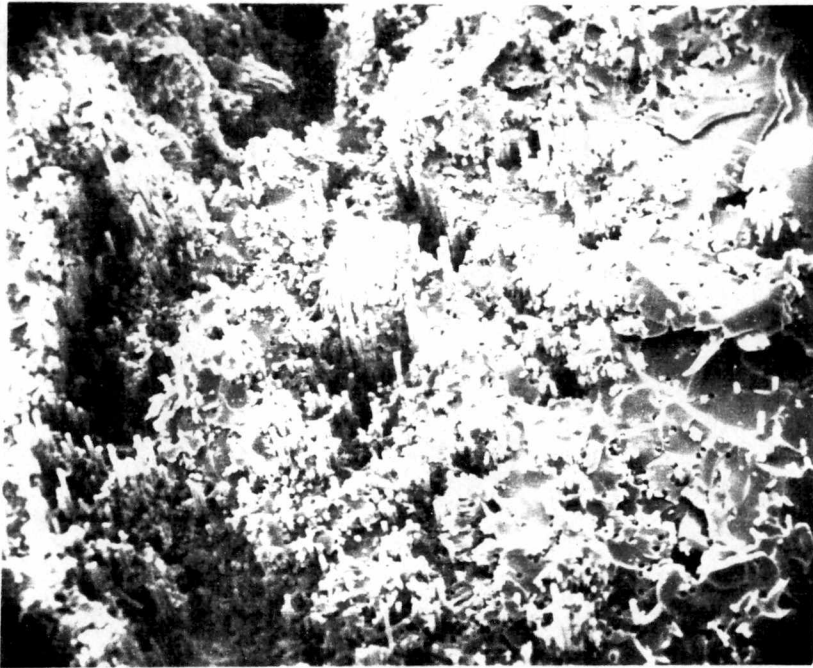


(c)

Figure 27 (continued)

Figure 28. The SEM of the fracture surface of
AS4/epoxy composites - under tension

- (a) 100x - 13% fiber volume fraction
- (b) 200x - 16% fiber volume fraction
- (c) 500x - 21% fiber volume fraction
- (d) 1000x - 13% fiber volume fraction
- (e) 1000x - 16% fiber volume fraction
- (f) 1000x - 21% fiber volume fraction
- (g) 5000x - 16% fiber volume fraction
- (h) 5000x - 21% fiber volume fraction

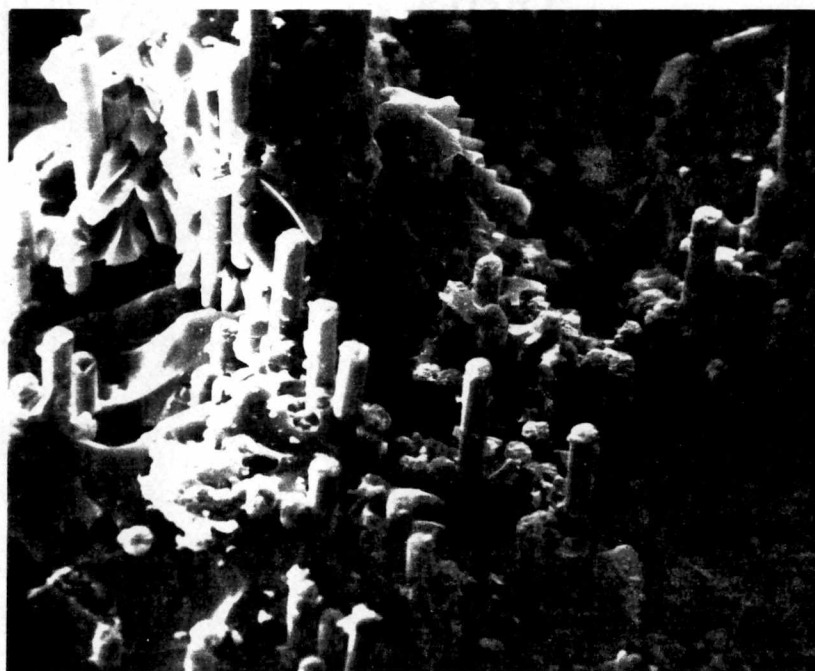


(a)

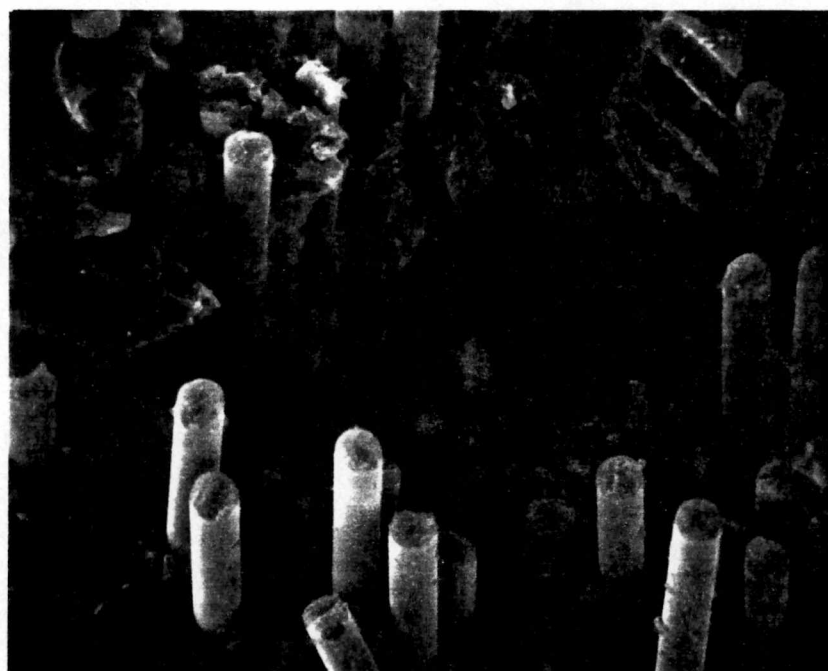


(b)

Figure 28 (continued)

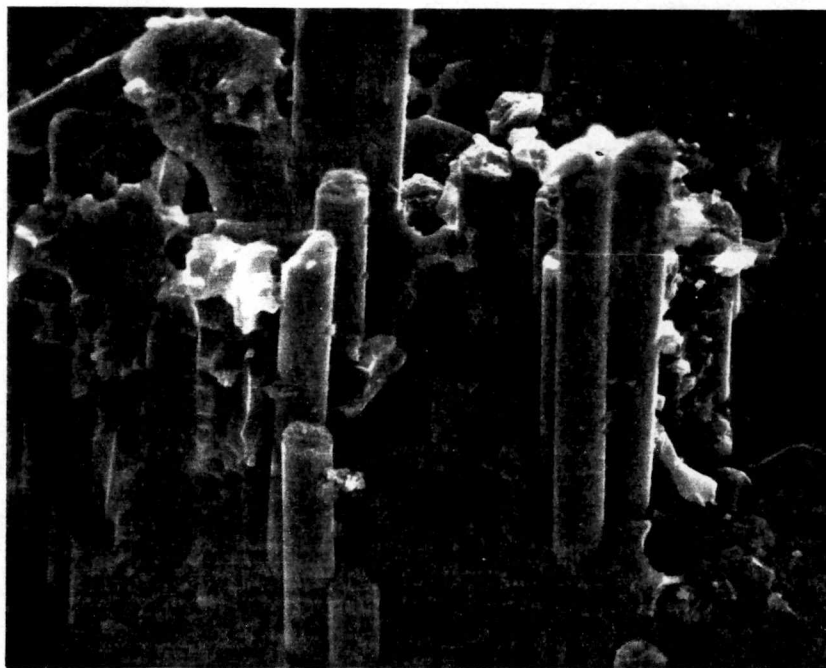


(c)

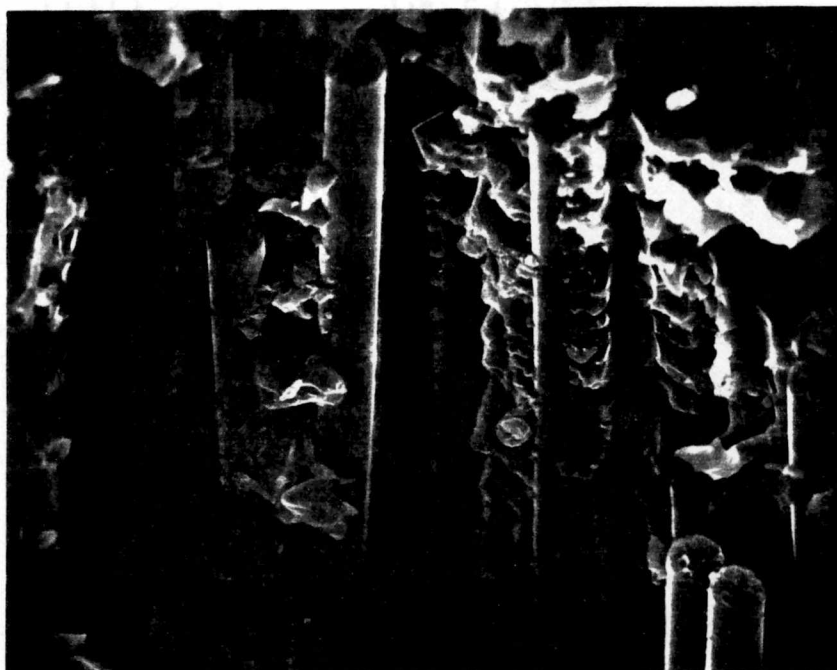


(d)

Figure 28 (continued)



(e)

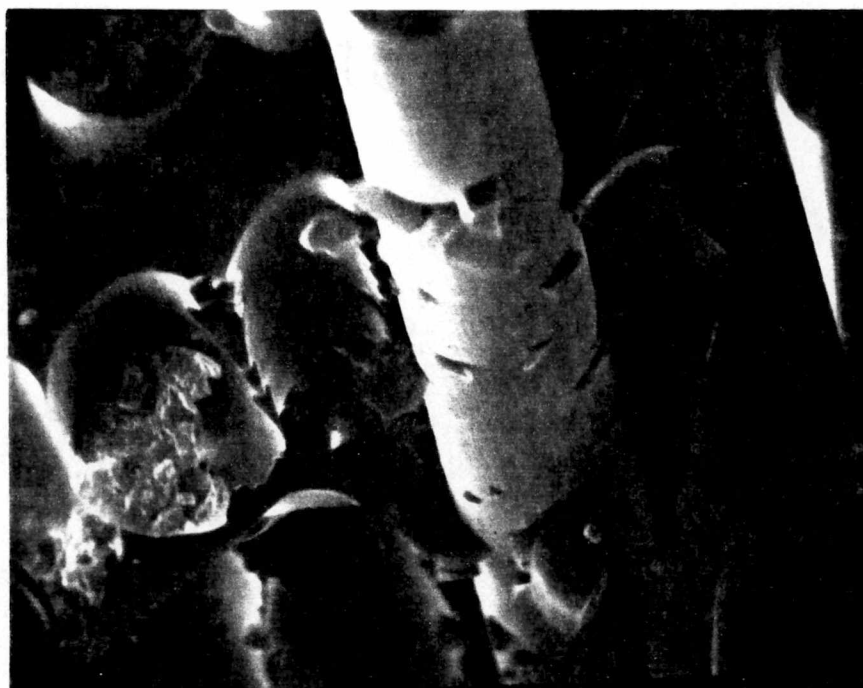


(f)

Figure 28 (continued)



(g)



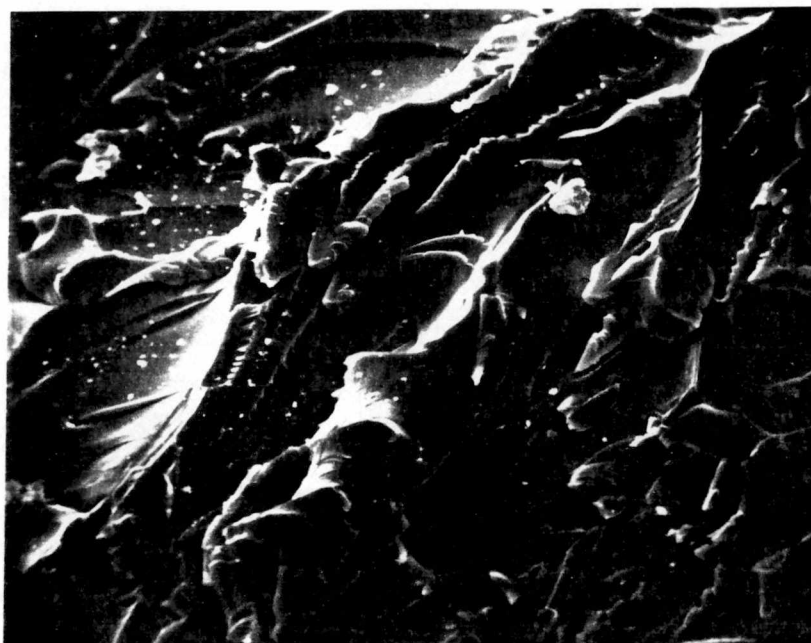
(h)

Figure 28 (continued)

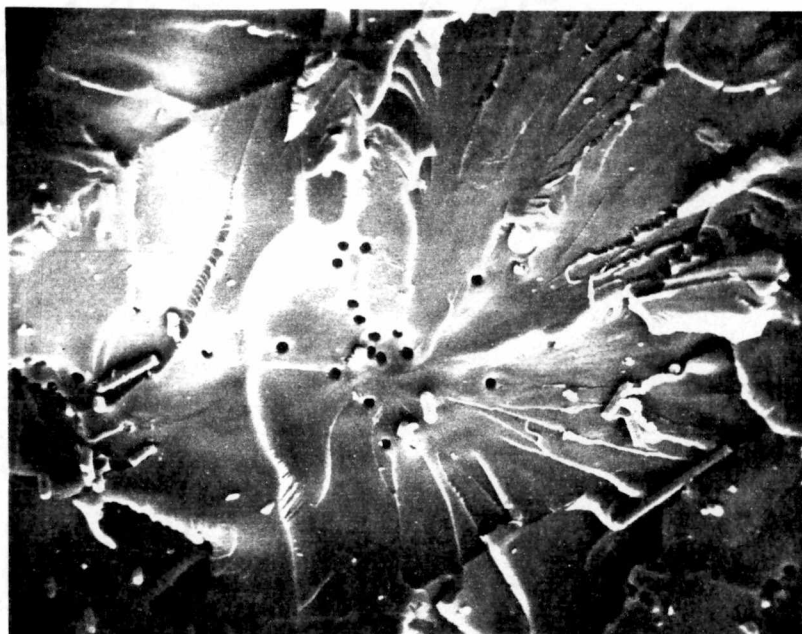
debonding. Such a failure process causes the crack to deviate from the original path. Thus, the fracture surface roughness in Figure 29(a) allowed the matrix to deform and absorb energy long beyond the yielding point. Figure 29(b) shows the crack was initiated from a broken fiber tip[45,51,90] and propagated into the resin matrix.

Two extreme cases are generally encountered in interfacial failure mode - poor interfacial bonding and strong interfacial bonding. In the case of poor interfacial bonding, fiber pull-out was observed, indicated by poor mechanical properties. At high interfacial strength from composites with surface treated carbon fiber, composite shear strength was high, but failure could be very catastrophic[42,43,44]. Thus, in order to get better mechanical properties and to avoid brittle catastrophic failure, optimization is needed between two extreme cases - poor and strong interfacial bonding. From the results of bending tests and tensile tests, AS4/epoxy composites showed relatively high ILSS(delamination) and high tensile strength(ductile plastic deformation), suggesting that these composite had almost optimum bond strengths.

The fracture surfaces of VSB-16/epoxy composites are shown in Figure 30. A low magnification picture of a typical failure surface is presented in Figure 30(a). At higher magnifications in Figures 30(d-h), VSB-16/epoxy composites



(a)



(b)

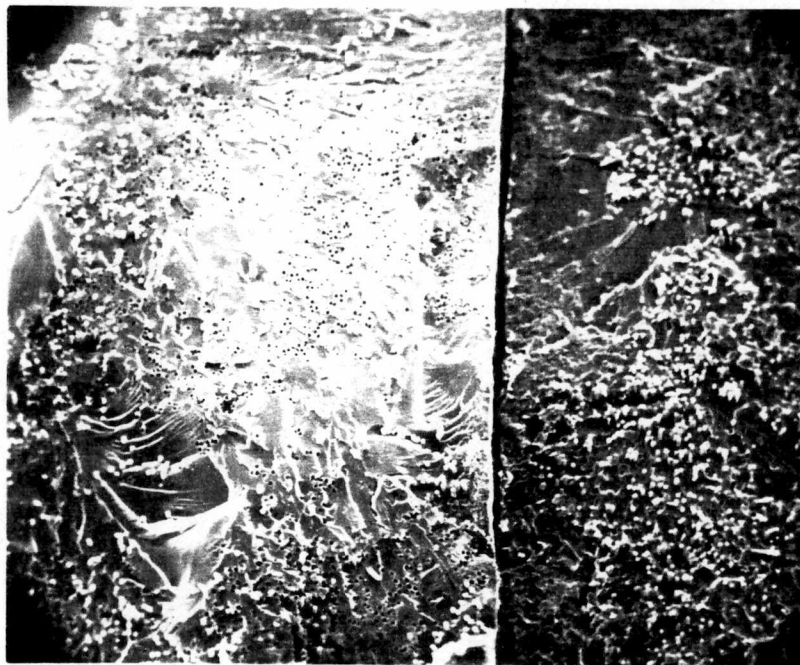
Figure 29. The SEM of the fracture surface of AS4/epoxy composites.

(a) 200x - 13% fiber volume fraction

(b) 200x - 16% fiber volume fraction

Figure 30. The SEM of the fracture surface of
VSB-16/epoxy composites - under tension.

- (a) 50x - 13% fiber volume fraction
- (b) 100x - 15% fiber volume fraction
- (c) 200x - 20% fiber volume fraction
- (d) 500x - 27% fiber volume fraction
- (e) 1000x - 15% fiber volume fraction
- (f) 1000x - 27% fiber volume fraction
- (g) 1000x - 13% fiber volume fraction
- (h) 2000x - 20% fiber volume fraction

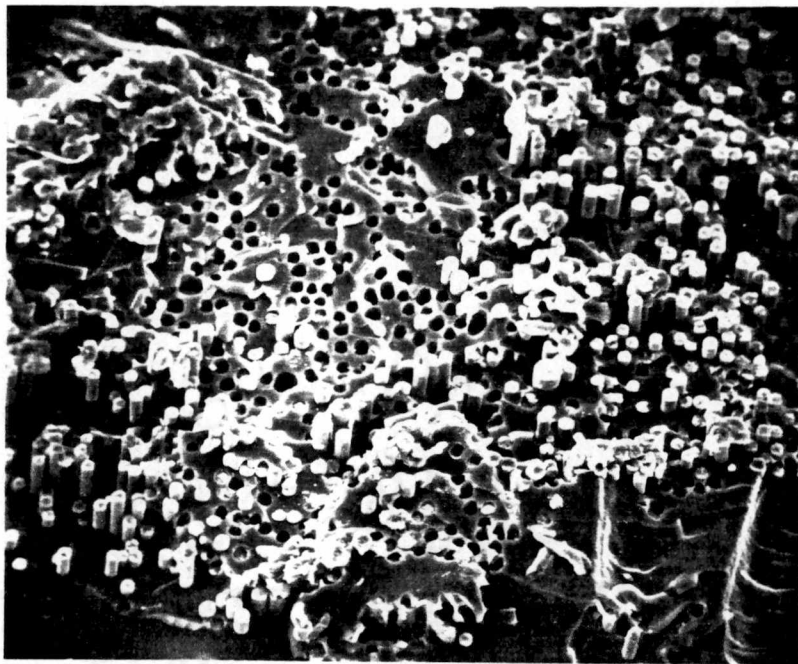


(a)

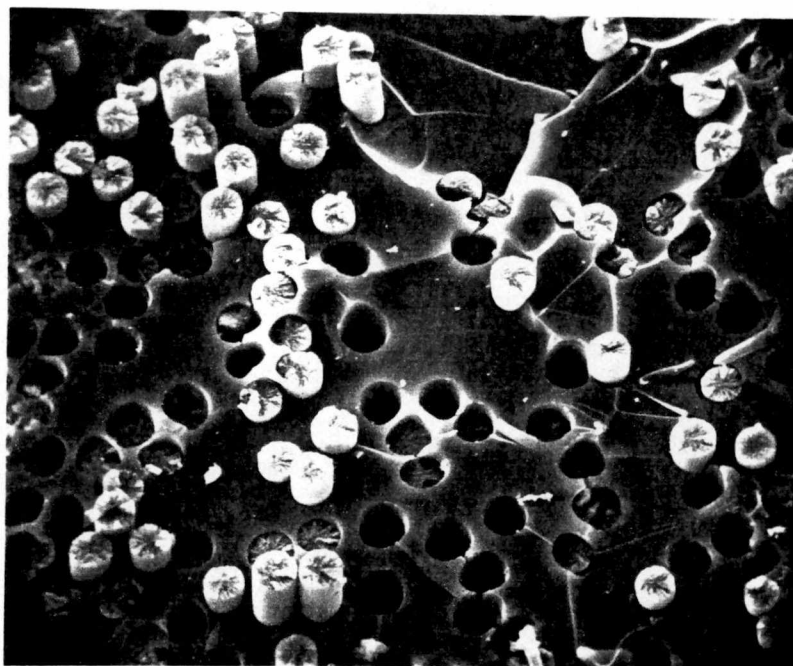


(b)

Figure 30 (continued)

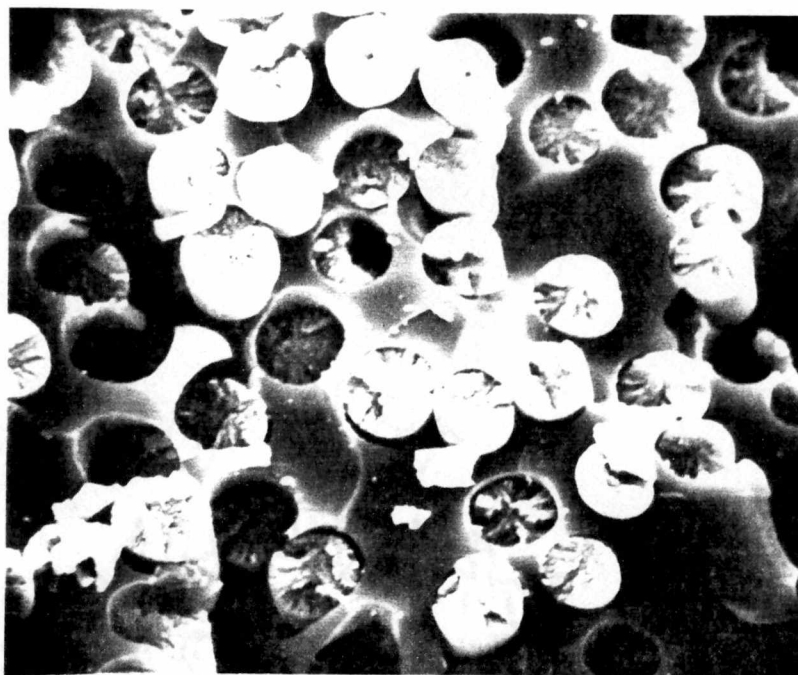


(c)

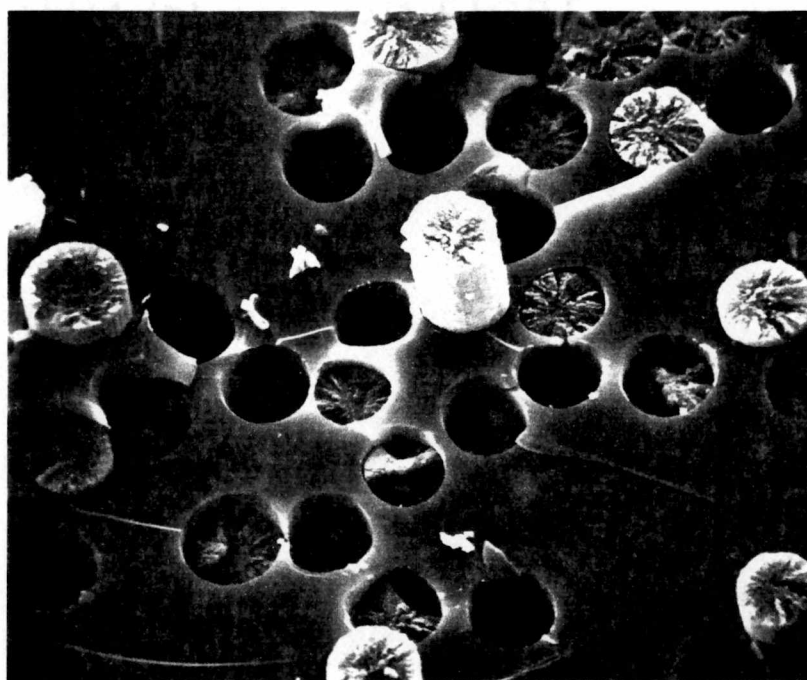


(d)

Figure 30 (continued)

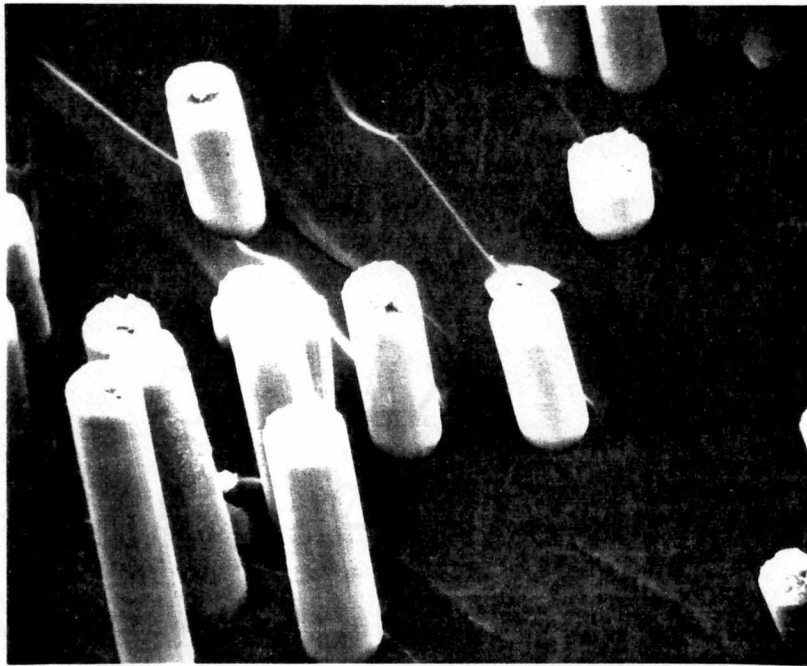


(e)

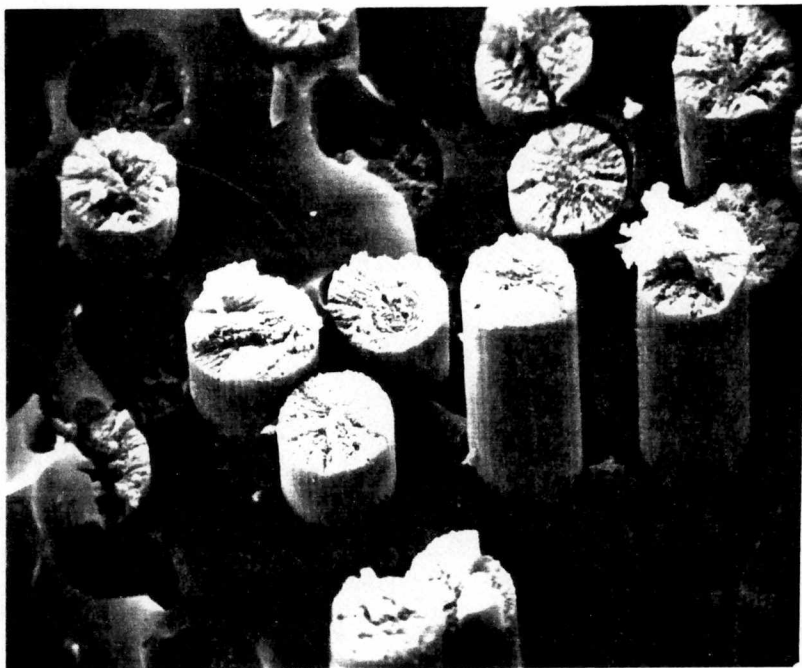


(f)

Figure 30 (continued)



(g)



(h)

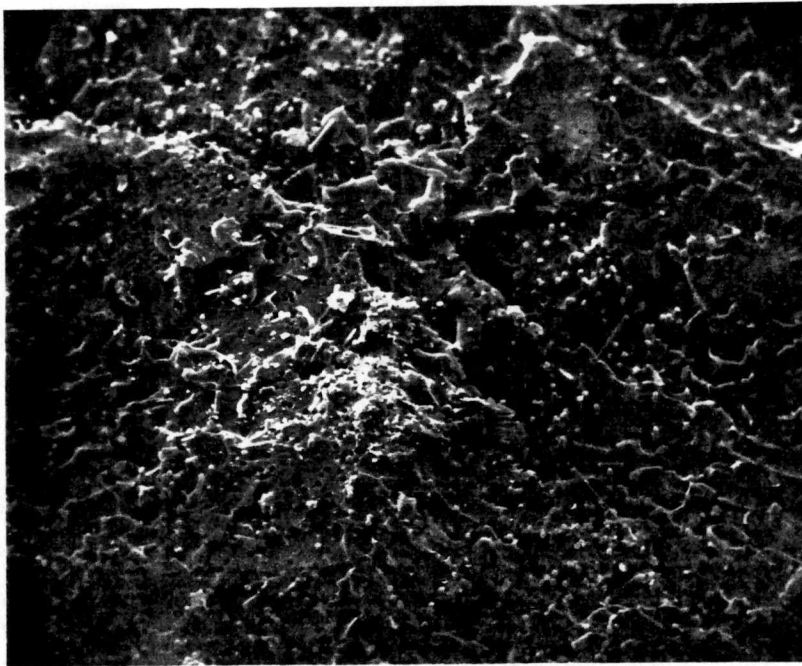
Figure 30 (continued)

generally show single fiber pull-out, instead of fiber bundle pull-out with epoxy, producing very clean and smooth fracture surface contrary to the AS4/epoxy composites. As shown in Figure 30(b) and 31(e and f), the crack originated from the broken fibers (brittle fiber to ductile matrix) and propagated into the matrix. The fracture surfaces of HMS/epoxy composites are smooth in some specimens and very rough in some specimens showing intermediate surface condition of AS4/epoxy and VSB-16/epoxy composites.

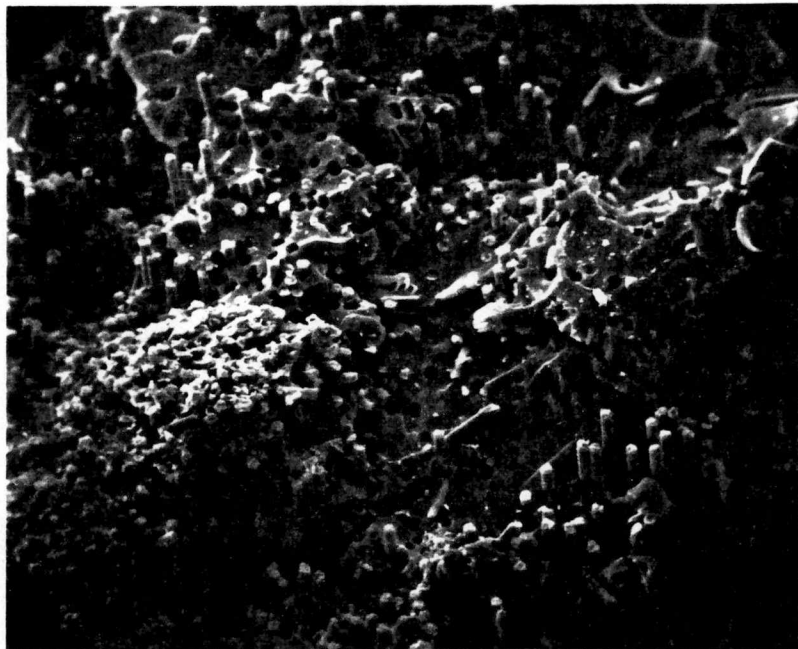
Comparing the fracture surfaces of AS4/epoxy composites with those of VSB-a16/epoxy composites, AS4/epoxy composites, showing ductile plastic deformation, were damaged (very rough fracture surface) much larger region above and below the main crack than VSB-16/epoxy composites, showing brittle catastrophic failure (very clean and smooth fracture surface) [53,54]

Figure 31. The SEM of the fracture surface of
HMS/epoxy composites - under tension.

- (a) 100x - 13% fiber volume fraction
- (b) 200x - 21% fiber volume fraction
- (c) 500x - 9% fiber volume fraction
- (d) 500x - 13% fiber volume fraction
- (e) 200x - 21% fiber volume fraction
- (f) 500x - 9% fiber volume fraction

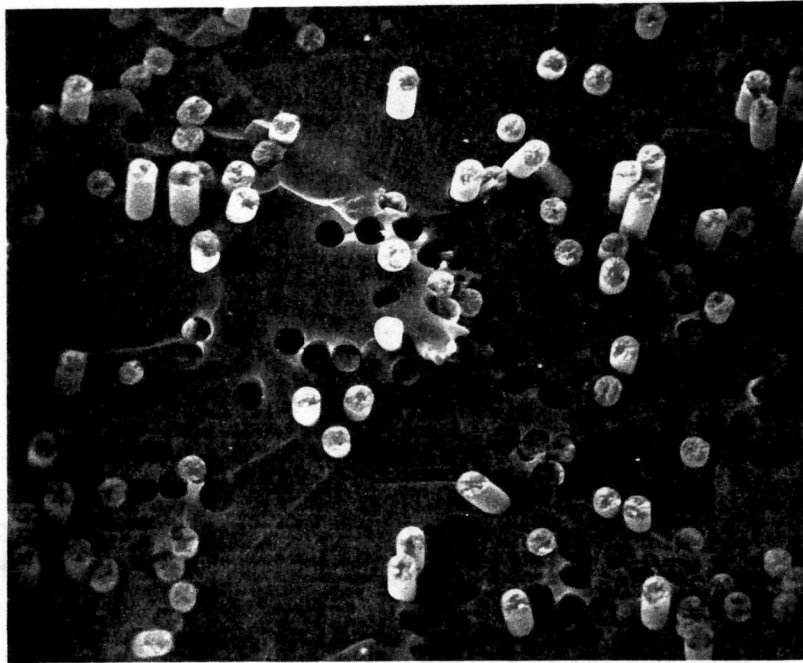


(a)

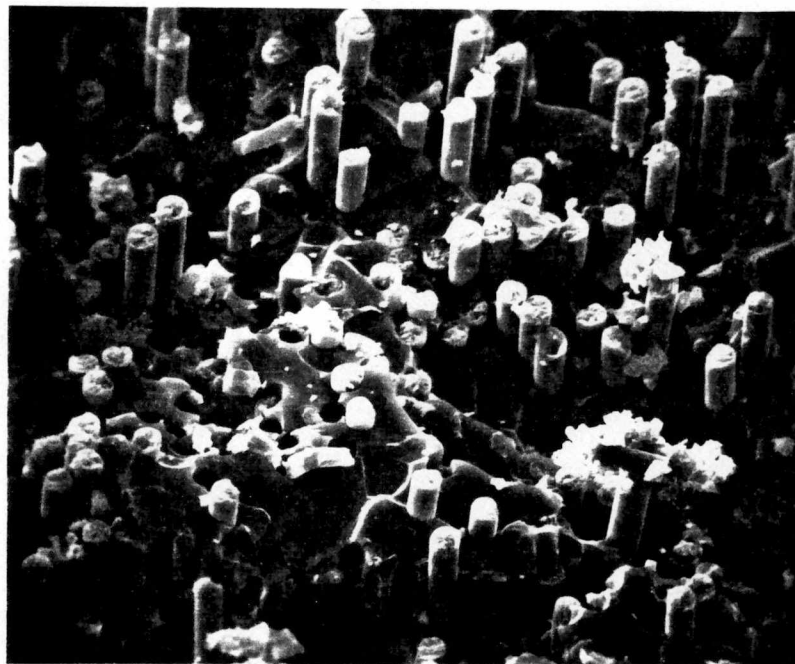


(b)

Figure 31 (continued)



(c)

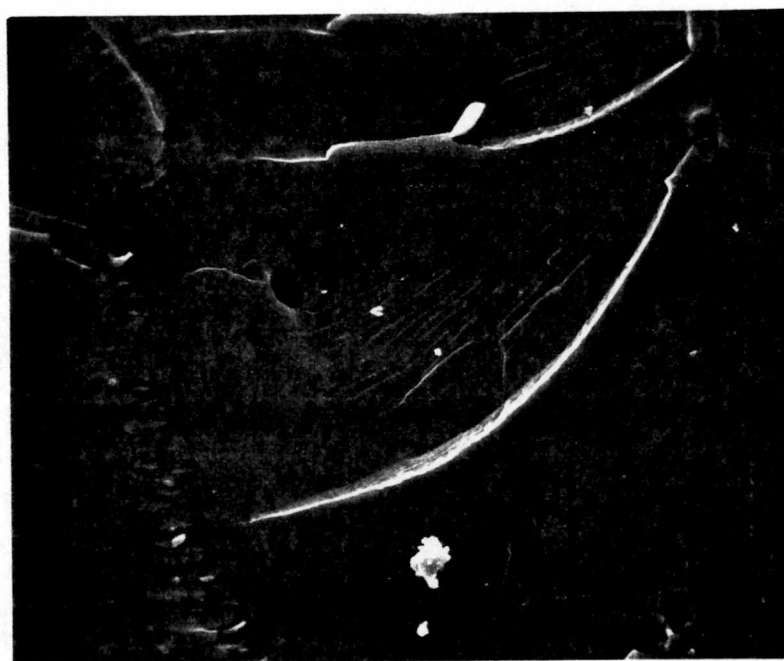


(d)

Figure 31 (continued)



(e)



(f)

Figure 31 (continued)

V. CONCLUSIONS

The ILSS of unidirectional graphite fiber/epoxy resin composites did not change greatly with etching time of 0-4 min. This results indicate that surface treatment with gas plasma was not so effective on the ILSS of graphite/ epoxy composites, contrary to our expectation from the literature review[82]. This is caused by the fact that the etched fibers showed almost no change in fiber surface with 0-4 min plasma etching. However, the ILSS changed with fiber volume fractions and showed maximum points at some fiber volume fraction. This existence of the maximum values for the ILSS indicates that there exists optimum fiber volume fraction for the reinforcing effectiveness to improve the ILSS.

The tensile strengths and moduli of the composites increased as the volume fraction of fibers increased. Two cases of failure mode were observed in this study; i) ductile plastic deformation by the PAN-based AS4/epoxy composites, ii) brittle catastrophic failure shown by the pitch-based VSB-16/epoxy composites. Even if the matrices of both cases were the same, the final failure modes were not the same due to the difference of the intrinsic characteristics of the fibers. The percent elongation of AS4/epoxy composites was much higher than that of individual components, i.e., the epoxy and the fiber. This interesting

feature is represented in the stress-strain curves of AS4/epoxy composites showing yielding. The ductile deformation accompanied by the yielding resulted from shear stress concentration due to the fiber breakage. This ductile failure is considered to absorb the fracture energy of the fiber, suggesting that matrix deformation accompanied by fiber breakage is considered to contribute to the fracture toughness of AS4/epoxy composites. The percent elongation of VSB-16/epoxy composites is lower than that of individual components and showed brittle catastrophic failure.

The SEM micrographs of fibers and fracture surfaces of composites showed good agreement with the results of mechanical tests. The most characteristic features of interlaminar shear failure surface of AS4/epoxy composites were delamination and formation of hackles. By forming the hackles and delamination of interface, AS4/epoxy composites relieved the stress concentration around fiber caused by the fiber breakage and showed much higher ILSS values than those from VSB-16/epoxy composites. Whereas VSB-16/epoxy composites under bending showed only tensile (or compressive) failure suggesting that the crack propagate very fast after some fiber breakage and lead to complete failure at relatively low stress. The principal fracture features of AS4/epoxy composites under tension were fiber

pull-out (single fibers and bundles) and very rough fracture surface due to the pull-out of fiber bundles with epoxy. This fracture surface roughness allowed the matrix to deform and absorb energy long beyond the yielding point by deviating crack from the original path and relaxing the stress concentration of the AS4/epoxy composites. Whereas VSB-16/epoxy composites generally showed single fiber pull-out, producing very clean and smooth fracture surface of composites.

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APPENDIX

Sample Calculation of Volume Fraction of Fiber

1. Before fibers were wound uniaxially around mold base,
measure the weight of mold base ; 197.8g
2. Before an aluminum frame was screwed on to the base,
measure the weight of
mold base + total fiber weight ; 207.2g
3. Total fiber weight ; 9.4g

After curing, demolded the composite sheet, and the composite sheet were trimmed as shown in figure 2.

4. Measure the weight of the composite sheet used ; 6.5g
[weight of (fiber + epoxy) used]
5. Measure the length of fiber used.
(length of composite sheet used); 3.22 inch
6. Measure the fiber weight used in composite sheet;

$$= \frac{\text{length of composite sheet}}{\text{length of around of the mold base}} \times \text{total fiber wt.}$$

$$= \frac{3.22 \text{ in (from 5)}}{(6 + 0.1) \times 2 \text{ in (from figure 1)}} \times 9.4 \text{ (from 3)}$$

$$= 2.48\text{g}$$
7. Measure the epoxy weight used in composite sheet;

$$= (4) - (6) = 6.5\text{g} - 2.48\text{g} = 4.02\text{g}$$

Therefore, the fiber volume fraction is calculated as follows;

$$V_f = \frac{V_f}{V_f + V_m} = \frac{W_f/\rho_f}{W_f/\rho_f + W_m/\rho_m} = \frac{1.377}{4.873} = 0.282$$

In this case, the fiber volume fraction is 28.2 %.

Where V_m is the volume fraction of matrix; ρ_f and ρ_m are the density of the fiber and matrix, respectively; W_f and W_m are the weight of the fiber and matrix, respectively. The density of matrix is measured in a density gradient column.

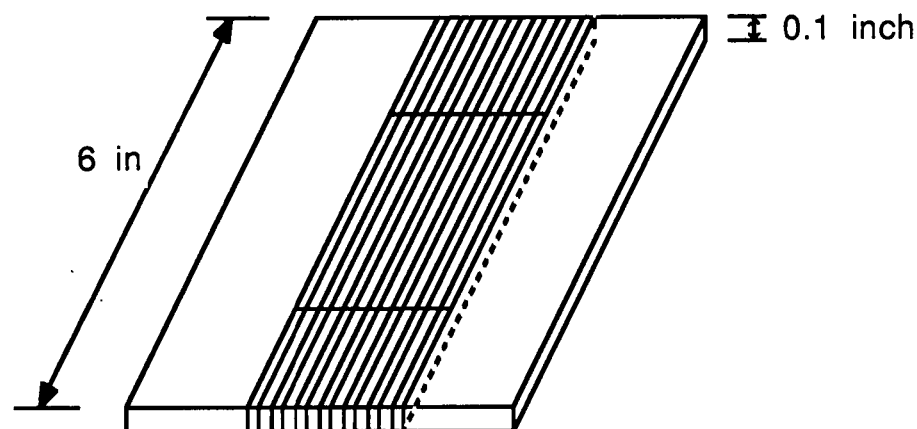


Figure 32. The dimension of mold base

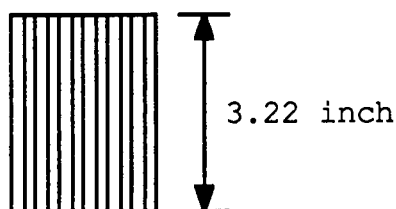


Figure 33. The dimension of composite sheet used

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