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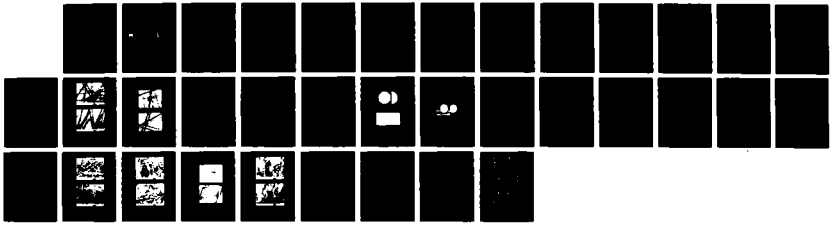

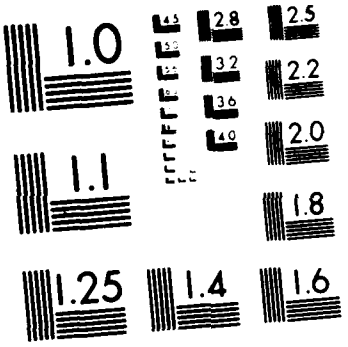

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SOL/GEL PROCESSING TECHNIQUES FOR GLASS MATRIX COMPOSITES

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November 1987

Final Report

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This report summarizes the first year of a two-year effort on sol/gel processing techniques for glass matrix composites. The emphasis in this program is on sol/gel fabrication techniques and their influence upon the composite properties. The program did not try to develop new matrices or reinforcements. Special emphasis was placed on the reduction in processing temperature and more uniform distribution of the glass matrix between the fibers.

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I. Introduction

Glass-matrix composites are of considerable interest for a variety of applications where dimensional stability, high stiffness and increased strength or fracture toughness are required. But, the standard techniques for processing glass-matrix composites face a variety of problems associated with both the glass matrix and the fiber reinforcement. The composite must be processed at high temperature, in the vicinity of Tg, to ensure distribution of the glass matrix, as well as viscous sintering and consolidation of the fritted glass slurry. Thus, appropriate time-temperature-pressure cycles, temperature uniformity and atmosphere control are critical to achieve densification without devitrification. This is an especially severe limitation for the higher temperature glasses such as silica and silica-titania. Moreover, high temperatures can be physically damaging to the fiber reinforcement, especially to carbon, which otherwise possesses the appropriate thermomechanical characteristics for achieving stiff, low thermal expansion glass composites. The bonding between glass matrix and fiber reinforcement must be optimized for composite strength and toughness. High strength composites require a strong bond between the fibers and the matrix glass while high toughness composites dictate a low degree of bonding. Therefore, glass matrices and fiber reinforcements must be chosen which are chemically compatible and yield the desired composite properties.

The objective of the present program is to enhance the processing and properties of glass-matrix composites using solution/gelation techniques; i.e., by hot-pressing fiber-reinforced gels. Sol/gel processing of the glass-matrix can provide many potential advantages for the fabrication of these composites; e.g.

(1) reduction in the processing temperature,

(2) ability to cast and mold complex shapes,

(3) access to a broad range of compositions which may be difficult or impossible to obtain by melt techniques,

(4) reduced tendency toward devitrification during processing due to lower processing temperatures and higher purity,

5) increased homogeneity and uniformity of the composite.

The emphasis in this program is on sol/gel fabrication techniques and their influence upon the composite properties, rather than the development of new matrices and reinforcements. Of particular interest is the reduction in processing temperature and more uniform distribution of the glass matrix between the fibers.

The hot-pressing of high-silica gels to produce dense, optical quality glass has not been extensively studied, but is an essential aspect of the fabrication of these composites. Thus, **(1)** identification of SiO_2 and TiO_2--SiO_2 gel formulations which are sufficiently homogeneous to prevent devitrification during hot-pressing, **(2)** development of a time-temperature-pressure schedule to produce optical quality glass by hot pressing gels, and **(3)** determination of the associated densification kinetics, have been addressed as an individual tasks and are presented in section II. Subsequently, section III describes the results concerning the composite fabrication and their properties. In this task, the glass matrix is a Pyrex composition - prepared by a sol/gel method - and the fiber-reinforcement is carbon. The Pyrex composition was used in this initial work because it facilitated the development of a general technique (i.e., Pyrex is less susceptible to devitrification than SiO_2 or TiO_2-SiO_2). In addition, the properties of these sol/gel derived composites can be compared directly with United Technologies' Compglas which utilizes a melt-derived Pyrex matrix.

II. Sintering, Hot-Pressing and Hot-Isostatic Pressing of Silica and Silica-Titania Gels

This effort is aimed at the preparation of 100% SiO_2 and 93% SiO_2-7%TiO_2 glasses via the densification of gels. Since the longe-range objective of this task is to develop a matrix precursor for low-expansion glass matrix composites, the behavior of these gels during hot-pressing (HP) and hot-isostatic pressing (HIP) are of primary interest. A key issue is the development of a chemical process wherein the sol does not undergo phase-separation and/or devitrification during gelation and drying, and similarly, the gel does not crystallize during the HPing or HIPing. The slow heating and cooling rates associated with HP and HIP render this latter point of special concern. Thus, the establishment of time-temperature-pressure schedules for optimum densification of the gel is a necessary objective. Altogether, the development of a sol/gel process for SiO_2 and SiO_2-TiO_2 - together with a data base for their densification - are prerequisite to the successful fabrication of glass composites with SiO_2 and SiO_2-TiO_2 matrices.

Background

Silica

Silica colloidal gels can be produced by dispersing particles smaller than 0.1 μm in either a polar or nonpolar medium. These colloids may be produced using a variety of techniques. Fumed silica powder with particles ranging from 10-40 nm in diameter, is produced by a flame hydrolysis method (e.g., Cab-O-sil or Aerosil) and has been found suitable for gelation. A gel is most easily produced by dispersing this colloidal silica in water at a pH of 2.7 or less. Often, though, these gels crack when dried at room temperature. Thus, Rabinovich et al. have developed the 'double process' technique for preparation of monolithic silica (Ref. 1). By crushing the first gel and redispersing it in water, a second gel with a bimodal pore distribution is obtained. This gel does not shrink or crack upon drying, and can be sintered to clear glass at temperatures between 1450 and 1500°C. Alternatively, Scherer (Ref. 2) has developed a technique which involves dispersing the colloidal silica in a nonpolar solvent such as chloroform. The use of a nonaqueous solvent helps prevent OH contamination, but primarily, it reduces the capillary stresses associated with aqueous gels and thereby reduces the tendency toward cracking. Finally, Shoup (Ref. 3) has developed a process wherein a soluble silicate is added to the sol(ution) before gelling. This forms silicic acid which improves gel bonding and controls the pore size distribution. The pore size in the final microstructure can be controlled through the solids loading of the sol to prevent cracking of the gels during drying.

In addition to the colloidal method, gels can also be produced through the hydrolysis of an organometallic compound (Ref. 4). However, the inherently small pore sizes and the large amount of organic material which must be removed from the gel before and during sintering limit the size of the casting. The large amount of solvent evaporation coupled with small pore sizes leads to sample shrinkage causing stresses which break the gel into small fragments upon drying. Additionally, these gels must be calcined at temperatures of 500°C for 24 hrs to remove all carbon residuals. Many glass systems begin densification at this temperature and often achieve closed porosity before all carbon is removed. Nevertheless, small pieces of silica gel made through this process have been sintered to full density at temperatures below 1200°C.

The colloidal method of gelation accommodates the fabrication of large silica structures while processing temperatures are still relatively low. Rabinovich, Scherer and Shoup have all been able to produce reasonably-sized gels which can be sintered to dense glass at temperatures at or below 1350-1700°C. In contrast, the formation of large monolithic glasses by the organometallic approach has been limited to sizes of the order 10 x 10 x 0.2 cm.

Titania

The only reported literature on colloidal gels in this system is due to Scherer and Pantano (Ref. 5) but their materials were always translucent due to the presence of microcrystallites. Otherwise, most of the reported literature concerns the use of organometallic precursors. The major obstacle to the preparation of these materials is the large difference in hydrolysis rate for titanium versus silica alkoxides. Thus, the tendency towards phase separation in the sol must be addressed.

The TiO_2-SiO_2 alkoxide gels have most often been produced by partially hydrolyzing a silicon alkoxide in an acidic water-ethanol solution (Ref. 6-9). After an aging time, the more reactive titanium alkoxide is added. This solution gels quickly and is ready to be further processed. This approach has the advantage of mixing titania and silica on a near'molecular level at room temperature. Of course, these gels still have the disadvantages associated with shrinkage, cracking and organic removal as described earlier. Pancrazi and his coworkers avoided these problems by calcining fragments of alkoxide derived gels and then hot pressing the gel-fragments to achieve full density (Ref. 9). Although they worked in the CaO-Al_2O_3-SiO_2 system, this approach could also be applied to the titania silica system.

Densification

Over 40 years ago, Frenkel (Ref. 10) proposed a two sphere viscous flow model which has been used as a foundation for glass sintering. In his model, Frenkel considers two stages of sintering, neck growth and pore collapse. In the neck growth region, the energy dissipated through the viscous flow of the body originates from the work of the surface tension forces which drives to reduce the surface area of the particles. The second stage of sintering is due to the collapse of isolated pores by capillarity. The reduction in pore size as a function of time (τ) according to his theory is:

$$r_o - r = \frac{\gamma}{2\eta}\,\tau$$

where r_o = initial pore radius

γ = surface tension

η = viscosity

Mackenzie and Shuttleworth (Ref. 11) derived a closed porosity model which is useful for the sintering of glass powders. This model also assumes that pore closure is due to capillarity. Their relationship is:

$$\frac{d(P/P_o)}{dt} = k(1-P/P_o)^{2/3}\,(P/P_o)^{1/3}$$

where

$$k = \frac{3}{2}\left(\frac{4\pi}{3}\right)^{1/3}\frac{\gamma n}{\eta}$$

P_o = theoretical density

P = bulk density

n = pores per unit volume

A recent open pore model by Scherer (Ref. 12) is also of practical importance. Scherer set the rate of energy dissipation due to viscous flow equal to the energy supplied by a reduction in surface energy. His equation for densification is:

$$\left(\frac{\gamma}{\eta l_o}\right)\left(\frac{P_s}{P_o}\right)^{1/3}\left(t-t_o\right) = \int_o^x \frac{2dx}{\left(3\pi-8\ 2\ x\right)^{1/3} x^{2/3}}$$

where $x = a/l$
a = unit length of cylinder
t_o = time when $x = 0$
p_o = initial density
l_o = initial length

His model is supported by experimental viscosity and densification data. All of these models show that the most important parameters controlling glass sintering kinetics are the initial pore size of the glass or gel and changes in glass viscosity due to changes in temperature, composition and sintering atmosphere.

Experimental Procedure

Silica

Two types of colloidal silica gels were studied: one produced by a standard silica dispersion and the other by a double-dispersion process. The standard silica dispersions or single processed silica gels were produced by dispersing 25 weight percent Aerosil 200 in water at a pH of 2.0. This gelled in a few hours and was then dried at room temperature. At this point, the gels could be used for sintering studies or double processed using Rabinovich's technique (Ref. 13). In this latter method, the single processed gels were crushed with a mortar and pestle and sieved for particle classification. These powders were calcined at 800°C for a period of 4 hrs before redispersing to 40 weight percent in water. The sol was cast in tubes and exposed to a vacuum to remove trapped air. The gelled samples were air dried for four days before sintering.

Alkoxide gels were produced using both acid and base catalyzed systems. Equal amounts of tetraethoxysilane (TEOS) and ethanol were mixed with HCl (0.0007 M) and one-quarter the amount of stoichiometric water. The temperature was maintained at 40°C for one day to partially hydrolyze the TEOS. The remaining water and/or ammonium hydroxide (for base hydrolyzed systems) were added to complete the hydrolysis step. The samples were gelled and dried at various rates to observe cracking.

Silica-Titania

A limited amount of cofumed titania/silica colloidal powder (5.7 mole percent titania) was supplied by Degussa. This powder was dispersed in water at a pH of 2.0, but did not gel until the mixture was exposed to an ammonia atmosphere for 1 hr. These single processed gels were dried in air (without cracking) in a period of 4 days.

Titania silica alkoxide gels were also produced by an initial partial hydrolysis of TEOS. After an aging period of 18-24 hrs, titanium (IV) isopropoxide was introduced, more water was added and then the mixture was agitated at 40°C for 1 to 2 hours. The sol to gel transition occurred within 2 1/2 hrs. The gels were dried in a microwave oven and then calcined at 500°C for 24 hrs to remove organics. The gelled pieces were then ball milled into a fine powder to be used for double-dispersion sintering and hot pressing studies.

Densification and Characterization

The gels were densified by conventional sintering, hot pressing and hot isostatic pressing. A rate of 1°C/min below 300°C was used during the sintering schedule to remove the surface hydroxyls. The optimum heating rate above 300°C was found to be 5°C/min for silica systems. Sintering experiments were performed in air or helium. The hot pressing experiments with pure silica were done with a simple press while the HIPing was carried out in a system manufactured by Autoclave Engineers, Inc. The characterization included Archimedes' density, mercury porosimetry, thermogravimetric analysis, particle size analysis (Horiba), SEM and XRD.

Results and Discussion

Silica

The acid catalyzed alkoxide sol/gels fragmented into small, clear pieces upon drying while basic systems became cloudy before gelation and powdered during drying. No attempt was made to densify these materials. Rather, they were used as gel-powder precursors for HPing and HIPing studies.

In the case of the colloidal gels, larger pieces could be fabricated, but nevertheless, cracking was a problem. The single-dispersed sols yielded large gel fragments which were 25% dense and had a bimodal pore size distribution. Other gels were produced by double-dispersion technique (using single dispersed gels ground into sizes ranging from 150 μm < 48 μm). These gels dried without cracking in air, and had a bimodal pore distribution which was affected by the size distribution of crushed material from which the gel was made.

The single processed silica gel was found to densify quicker and more completely than the double processed gel. The bimodal distribution of pores in the single processed gel had a large percentage of 75 Å pores and a smaller frequency peak of 1400 Å; the mean pore size was found to be approximately 88 Å. The double processed gel (-400 mesh) had a bimodal distribution of pores centered at 2000 Å and 86 Å with a mean pore size of 140 Å. According to the glass sintering theories, smaller and more uniform pore sized structures are expected to densify quicker. Thus, the single dispersed samples could be densified to clear glass at temperatures as low as 1150°C. The sintering data as a function of pore size and gel particle size can be found in Table 1.

The major problem encountered during densification was bloating of the gels. The bloating is apparently caused by the release of hydroxyl groups from the surface of closed pores at high temperatures. The tendency toward bloating could be reduced by calcining the crushed powders at 1°C/min below 300°C, and by keeping subsequent heating rates low. Lower sintering temperatures, careful drying and storage procedures, and the use of more finely ground powders in the second dispersion also helped prevent bloating. The single processed gels seemed more susceptible to bloating than the double processed gels, probably due to their smaller mean pore size and the absence of the intermediate calcination step. Sintering the gels in helium did not alleviate the bloating behavior of gels.

An alternative method of densification is the hot pressing of powdered-gel compacts. Thus, the single processed colloidal and alkoxide gels were ground with a mortar and pestle to less than 63 μm. A thermal expansion mismatch between the alumina dies and the silica glass led to failure of many samples upon cooling; however, some successes can be reported. Both the colloidal and alkoxide gels pressed at 1400°C and 7 MPa for less than 30 min resulted in clear glass. Some of the data from the hot pressing experiments is presented in Table 2.

Table 1.

Densification Behavior of Silica Gels

Precursor size for double processed gels	Mean pore size (Å)	Sintering temperature (°C)	Sintering time (min)	Percent theoretical density
Single processed	88	1150	60	100
Single processed	88	1300	30	99.8
Single processed	88	1300	10	96.0
Single processed	88	1400	10	bloated
180 μm-212 μm (double)	89	1250	60	95
106 μm-125 μm (double)	94	1250	60	95
38 μm-53 μm (double)	100	1250	60	99.6

Table 2

Densification Behavior of Cold-Pressed Silica Gel Compacts

	Temperature (°C)	Time (min)	Pressure (MPa)	Theoretical density
Colloidal	1400	25	6.9	100
Colloidal	1150	60	6.9	96
Colloidal	1200	45	11.7	82
Colloidal	1300	30	7.4	98
Alkoxide	1400	15	6.9	99

There was also some effort placed on densifying glass by the HIP method. To successfully HIP a sample, all porosity in the sample first must be sealed off from the pressurizing gas (i.e., Argon). A glass encapsulation can be achieved by dipping the sample in a viscous melt or by sealing a glass tube around the sample in a vacuum. A glass with the proper viscosity-temperature relation must be chosen and care must be taken to ensure that the encapsulation does not react with the sample. A metal can could also be welded around the sample and sealed off in a vacuum in a similar fashion. Another alternative is to densify the sample to closed porosity (~92% theoretical density) so that the sample is essentially self-encapsulated. In the

case of these gels, self-encapsulation was used to great success. The partially densified samples became fully dense at HIPing conditions of 1000°C and 100 MPa. A thin crystallized outer crust developed on all samples which could not be reduced under any conditions of temperature and pressure.

Silica-Titania

Efforts were initially concentrated on a small batch of cofumed titania silica powder supplied by Degussa. The gelation was accomplished by exposing the aqueous colloidal mixture to ammonia gas. The ammonia creates cationic bridges between the negative sites on the colloid surface in solution. These gels were made into cylinders 2.5 x 3 cm and did not crack upon drying. Although the glass became dense upon sintering at 1300°C, it remained opaque until HIPed at 1500°C. Due to the limited amount of material available, it was not possible to determine whether the opacity was due to inhomogeneities in the original powder or due to crystallization during sintering.

The alkoxide method produced a clear gel with no visible phase separation. The TGA showed that all organics could be removed at 500°C if the heating rate was slow. The gel fragments appeared to be clear after calcination, and were ball milled using alumina and zirconia media (impurity levels from the zirconia media were found to be less than 0.1 weight percent after 72 hrs of milling). Initially, it was hoped that these particles could be redispersed to form a colloidal gel, but the results to date are not promising. The milled powders had average particle sizes of 2-5 μm which may be too large to obtain a stable suspension.

III. Carbon-Fiber Reinforced Glass Matrix Composites

This portion of the effort is focussed on the preparation and characterization of composites. In all cases, the fiber-reinforcement is carbon, although a wide variety of carbon-fiber types were evaluated including chopped fibers, continuous fibers, fiber paper and woven sheets. The glass matrices have a Pyrex composition and were fabricated using the sol/gel process. The primary objective of this year's effort was to evaluate whether these composites could, in fact, be prepared using a sol/gel matrix. Of particular concern are **(1)** the extent of solids loading which can be achieved in the composite preform via sol/gel, **(2)** the effects - if any - of volatiles within the gel matrix during the drying and densification, and **(3)** the fiber/matrix interface created during the gel densification. The final microstructure and mechanical properties of these composites were characterized so that the performance of these sol/gel-derived composites could be compared with the frit-derived composites prepared at United Technologies Research Center.

Background

Fiber reinforced glass matrix composites were first reported in the early 1970's by Sambell, Phillips (Refs.14, 15, 16, 17). Both discontinuous and continuous carbon fibers were used to strengthen Pyrex glass and soda-lime glass. It was found that the fracture strengths of the discontinuous fiber reinforced glass matrix composites were increased when the fibers were partially aligned, and were decreased when the fibers were randomly oriented. In all cases, though, the work of fracture was increased compared to the nonreinforced glasses. A significant increase in flexural strength and in work of fracture was achieved when the glasses were reinforced by unidirectionally aligned continuous fiber. Strengths up to 680 MPa and a work of fracture as high as 3 kJm^{-2} were reported.

More recently, the development of fiber reinforced glass matrix composites has been extended mainly by Prewo at UTRC (Refs. 18, 19, 20, 21, 22, 23). A wide range of fibers and glass/glass ceramic matrices have been explored. The reinforcing fibers were silicon carbide, monofilament, silicon carbide fiber yarn, carbon fiber yarn and alumina fiber yarn. The commonly used matrices included Corning 7740 borosilicate glass (Pyrex), Corning 1723

aluminosilicate glass, Corning 7930 high silica glass and lithium aluminosilicate glass ceramics. Very high flexural strength and fracture toughness (for example, 830 MPa and 18.9 MPa $m^{1/2}$, respectively) have been obtained. These composites have many other outstanding properties required for high performance, such as low thermal expansion, low density, good resistance to thermal shock and machinability. These and other important research accomplishments have been well reviewed and summarized in the literature (Refs. 24-25). Due to the widespread interest in ceramic-matrix composites, in general, there has been a considerable effort to understand the toughening mechanisms in these materials (Refs. 26, 27, 28, 29, 30, 31). It has been found that the toughening mechanisms include load transfer from the matrix to fibers, matrix prestressing due to the thermal expansion mismatch between the matrix and fibers, crack impediment, crack deflection, crack branching and fiber pullout. In the case of carbon-fiber/glass matrix composites, fiber pullout is the most important mechanism.

At present, the most common method employed to prepare fiber reinforced glass matrix composites is slurry infiltration. In this process, fiber tows or preforms are impregnated with a slurry containing well ground glass powders (or frit), carrier liquids, organic binders and probably wetting agents. Subsequently, these impregnated preforms are dried and the binders are burnt-out. Finally, the preforms are cut to proper size, laid up in a die, and HP.

In contrast, the use of a sol/method to prepare these composites utilizes a sol(ution) to impregnate the fibers. Here, the oxide solids form within the solution via hydrolysis/ condensation during the gelation and drying of the preform (i.e., the alkoxide approach), or are introduced as submicrometer colloidal particles (i.e., the colloidal approach). In either case, one can expect a more uniform distribution of the matrix phase - at least in the preform - than is obtained using ~50 μm glass frit. A few researchers have already recognized the great potential of the sol/gel technique in composite fabrication. Mazdiyasni has explored a wide range of ceramic-matrix composites using sol/gel (Ref. 32). Fitzer and Gadow reported fracture strengths of ~950 MPa and fracture toughnesses of 10.5 MPa $m^{1/2}$ for composites based on SiC coated continuous carbon fiber in sol/gel-derived SiO_2 and Al_2O_3 matrices (Ref. 20).

Methods of Fabrication

Carbon Fibers

A variety of carbon fibers were used in this study including continuous fiber yarn and fiber fabric, discontinuous fiber paper and mat, and chopped fiber. The relevant properties and producers of the fibers are listed in Table 3. It was expected that the unidirectional fiber yarn reinforced glass matrices would possess an exceptionally high level of strength and toughness in the fiber axial-direction. The discontinuous fiber paper and mat reinforced composites, on the other hand, should yield reasonably high in-plane strength and toughness and two-dimensional isotropic behavior. Finally, the chopped fiber reinforced composites would, in principle, demonstrate three-dimensional isotropy with a measureable improvement in mechanical properties over glass matrices alone. So far, though, most of the work has been directed toward discontinuous fiber paper and mat reinforced composites.

Two types of the fiber paper were purchased from International Paper Company. They were made from the same carbon fiber (Fortafil 3). One paper was extremely thin with a thickness of about one fiber diameter and a density of 0.2 oz per square yard; the other paper was thicker with a density of 3 oz per square yard. Both papers utilize a two-dimensional array of randomly oriented (in plane) fibers of Fortafil 3 whose length is of the order 1 in. They are held together by approximately 7% polyester. The paper is one yard wide and is received in continuous lengths. A discontinuous fiber mat was obtained from Union Carbide wherein T-300 carbon fiber is used. Here, most of the fibers are randomly oriented in two-dimensions. But no sizing and organic binder are used to prepare these mats, and so they are very loose and spongy.

Table 3.

The Properties and Producers of Carbon Fiber Reinforcements

Fiber Form	Paper	Mat	Chopped	Fabric	Yarn
Fiber Producer	Great Lakes	Union Carbide	Union Carbide	Union Carbide & Celenese	Union Carbide
Fiber Trade Name	Fortafil 3	Thornel -300	Thornel -300	Thornel-300 & Celioon 1000	Thornel -300
Diameter (μm)	Peanut shape of cross section	7	7	7	7
Average Length (cm)	2.5	-	0.25-1.0	Continuous	Continuous
Young's Modulus (GPa)	207	234	234	234	234
Ultimate Tensile Strength (GPa)	2.48	2.93	2.93	2.93 and 2.76	2.93
Thermal Expansion Coefficient (10^{-6}/°C)			-0.4 to -1.8		
Density (g/cm^3)	1.73	1.76	1.76	1.76	1.76
Binder Coating	Yes Polyester	No	No	Yes	No

The SEM micrographs in Figures 1 and 2 show that these papers (International Paper and Union Carbide, respectively) are, in fact, comprised of individual fibers. Figure 2 shows the surface morphology usually associated with oxidized carbon fiber which indicates a difference in surface chemistry for these two fiber-types, as received.

Glass Matrix

The glass matrix has a borosilicate composition (also known as Pyrex) i.e., $81SiO_2$, $2Al_2O_3$, $13B_2O_3$, $4Na_2O$ by weight. Some properties of this glass, as well as silica-7% titania, are shown in Table 4. The composition and properties of the glass matrix can directly influence the elastic modulus, thermal expansion coefficient, and maximum service temperature of the composite. The chemical composition of the glass matrix may be of critical importance in determining any reaction with the carbon fibers during hot pressing. This can affect the fiber/matrix interface, and thereby, determine the overall performance of the composite. It has been demonstrated repeatedly by Prewo (UTRC) that Pyrex glass is chemically compatible with the carbon fiber.

Tetraethoxysilane (TEOS), trimethyl borate aluminum s-butoxide and sodium acetate are used as starting materials to introduce SiO_2, B_2O_3, Al_2O_3 and Na_2O compositions into the sol/gel. The solution preparation procedure is shown in Figure 3. First, the calculated amount of TEOS is mixed with an equal volume of ethanol solvent. The specific amount of TEOS used in each synthesis is dependent upon the predetermined quantity of matrix material (i.e., solids) desired in the composite preform. The mixture is stirred with a magnetic bar and one-quarter of the quantity of water required to fully hydrolyze the TEOS is added to this solution; several drops of 1 M HCl solution are added to catalyze the hydrolysis. The sol is heated and held at 60°C for 30 min. It is then cooled to 40°C before the proper amount of aluminum s-butoxide (dissolved in isopropanol at 50 vol%) is slowly added to the solution; an additional quantity of water is also added at this time. After 5 minutes, trimethyl borate is introduced to the solution with the temperature held at 40°C. At this stage, the total addition of water is around 25% of the theoretical amount needed to completely hydrolyze all of the metal alkoxides. (The rationale for this partial hydrolysis is the desire to maintain compositional homogeneity.) About 30 min later, more water and a little acetic acid are added. Finally, the 2 M sodium acetate solution is slowly incorporated and then the solution is further mixed. In the final sol, the water content is 2.2 times the stoichiometric amount required for the full hydrolysis of the alkoxides added. The logic used here is that the excess of water will drive the hydrolysis to completion and, thereby, displace alkyl group from the network of the gel. Thus, it should be possible to eliminate these volatile organics from the matrix during the initial heat treatment of the composite preform.

Chopped Fiber Composites

Chopped fibers with lengths of 2.5, 5, and 10 mm were obtained by cutting T-300 fiber yarn. The key step in this process is uniform dispersion of the chopped fibers within the sol(ution). It was learned after many experiments that the viscosity of the sol played the most important role in determining the extent of dispersion. If the viscosity of the sol was too low, the chopped fiber bundles agglomerated together and could not be individually separated by magnetic stirring. On the other hand, if the sol was too viscous, the fiber could not be effectively stirred in the sol. The best dispersion results were achieved at the viscosity where gelation was just beginning. At this time, the chopped fibers could be gradually added to the sol while continuously stirring. It takes several minutes to ensure the uniform distribution of the fibers in the sol. Afterwards, the mixture is sufficiently fluid so that it can be poured into a plastic mold. A mold release agent (Union Carbide R-272 organisilane ester) is used to reduce the cracking of the composite preform during gelation. The dish is held in the laboratory atmosphere and gelation occurs within 30 min.

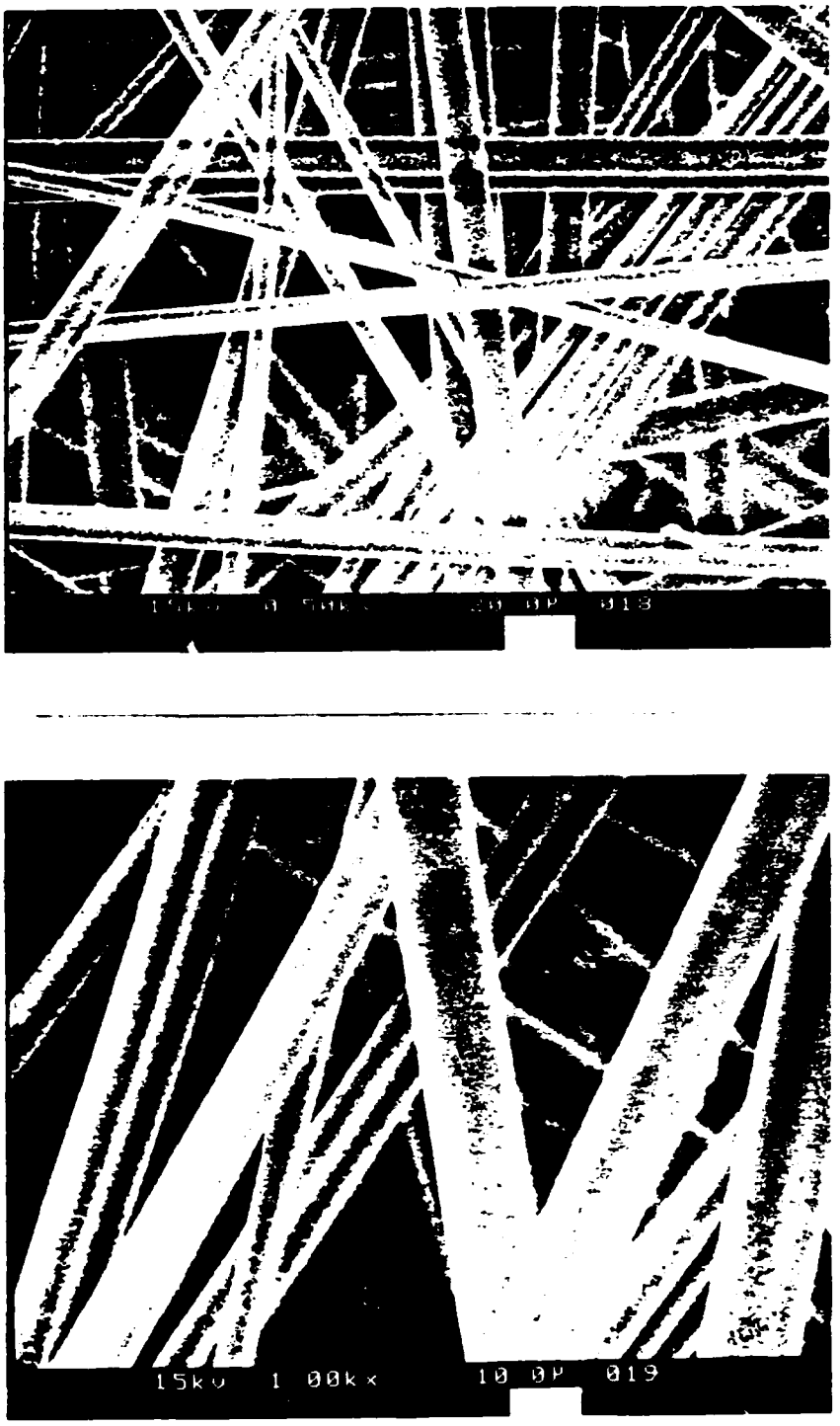


Figure 1. SEM Micrographs of Discontinuous Carbon Fiber Paper (International Paper Co.).

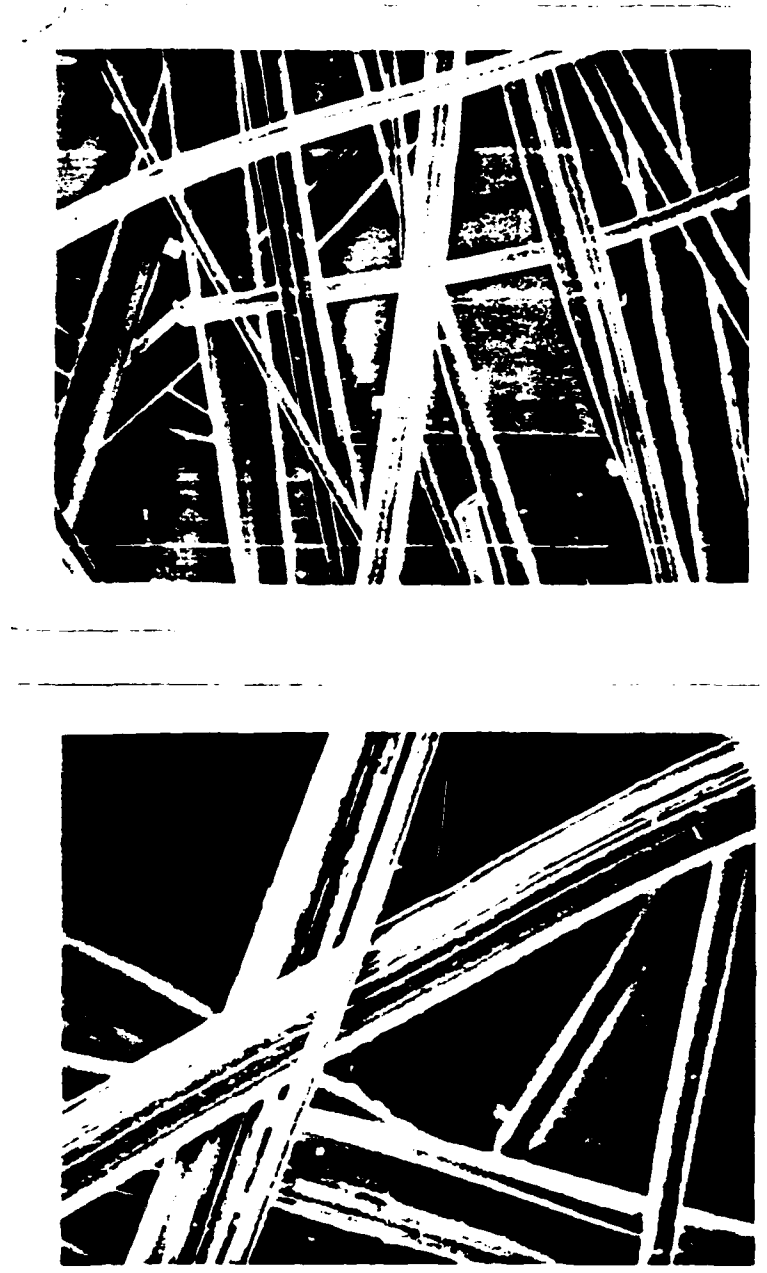


Figure 2. SEM Micrographs of Carbon Fiber Mat (Union Carbide); Note Oxidized Surfaces.

Table 4.

Glass Matrix Properties

Glass	Borosilicate	Titania Modified Silica
Annealing Point (°C)	560	1000
Softening Point (°C)	820	1500
Elastic Modulus (GPa)	63	68
Tensile Strength (MPa)		
Coefficient of Thermal Expansion (10^{-6}/°C)	3.25	0.05
Density (g/cm^3)	2.23	2.21

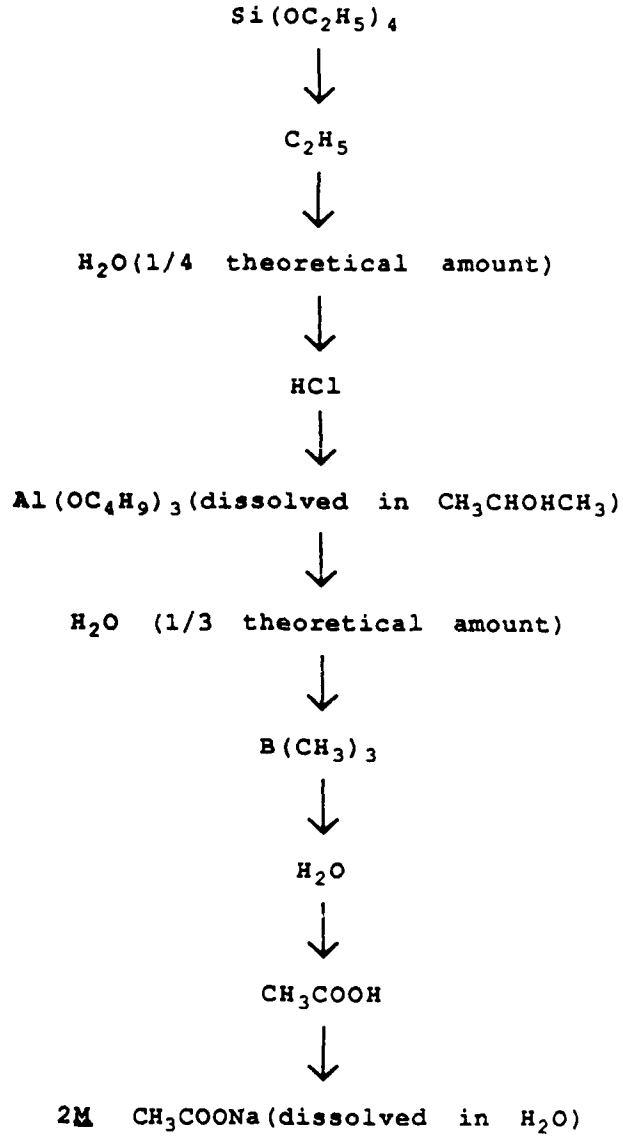


Figure 3. A Flow Chart of the Borosilicate Sol/Gel Glass Preparation Method.

The chopped fiber could be incorporated into the sol over a range of 1 to 10 volume percent. It was noted that addition of the chopped fiber to the sol significantly reduced the shrinkage and macrocracking of the gel.

Discontinuous Fiber-Paper and Fiber-Mat Reinforcements

The preparation of composite preforms using fiber-paper proved to be exceedingly straightforward via sol/gel processing. A wide range of fiber fractions could be incorporated in the matrix because the solids content of the sol could be simply adjusted through the quantity of alcohol solvent used. The volume percentages of the fiber paper or mat used in this work varied from 10 to 60. It was found that sol used with the paper or mat form of carbon fiber should be much less viscous than the sol used with the chopped fiber, otherwise complete penetration and wetting would not occur.

In practice, the paper and mat are cut into the desired size and then are placed in the mold - which already contains the fluid sol - ply by ply to make sure that the sol has already wetted the underlying ply before loading the next one. More sol can be added later if necessary. After about 2 hrs at room temperature, the gelation would begin.

It was concluded that another important advantage of using the paper or mat as a reinforcement is the absence of lateral shrinkage. The composite preform, in this case, did not shrink in-plane where the fibers were oriented. All of the shrinkage during gelation and heat treatment occurred in the direction normal to the fiber ply. This offers one the opportunity to make near-net shapes. Also, macrocracking did not occur in this kind of composite preform due to the skeletal role played by the in-plane randomly oriented fiber. Therefore, the preform could be made into any desired size. Figure 4 shows some samples of the preform (i.e., after impregnation, gelation, drying and pre-heat treatment).

Continuous Fiber Yarn Reinforcement

Although the processing of the cloth and paper was carried out in a comparable fashion, an important difference is that the fabric is much more dense and heavy than the paper. Therefore, whereas the paper could almost be suspended in the sol, the fabric tended to fall to the bottom of the mold. This led to difficulty in evenly distributing the fabric. The method used to overcome this problem was to load a ply of paper between every two plys of cloth. This prevented sedimentation of the cloth fabric and led to more uniform distribution of the fabric in the mold. The gelation and shrinkage behaviors of the cloth fabric reinforced sol/gels are approximately the same as those for the paper reinforced sol/gel.

Continuous Fiber Yarn Reinforcement

These composites were fabricated with 50 vol % of unidirectionally aligned T-300 continuous fiber yarn. The fiber yarn was cut to predetermined lengths. These strands were laid-up in parralel and fixed with tape at the ends. Also, a gap was left between each strand, usually 3-5 mm, to allow the sol to readily penetrate the fiber, but more so to provide space for the individual fibers to spread out during later hot pressing. Again, the fiber tow tended to settle at the bottom of the mold, and some fiber paper was loaded between the fiber strand plies to maintain their suspension until gelation.

Pre-Heat Treatment of the Composite Preforms

The heat treatment (or calcining) of gels is a necessary step to remove water and residual organics. Also, this heat treatment is one of the greatest challenges to researchers who aim to prepare large monolithic materials since, in most cases, the gel cracks due to high local shrinkages. However, cracking was not a problem during the heat treatment of these composites. Because of the fiber reinforcement in the gel matrix, the matrices microcracked, but in no cases did the preform fail.

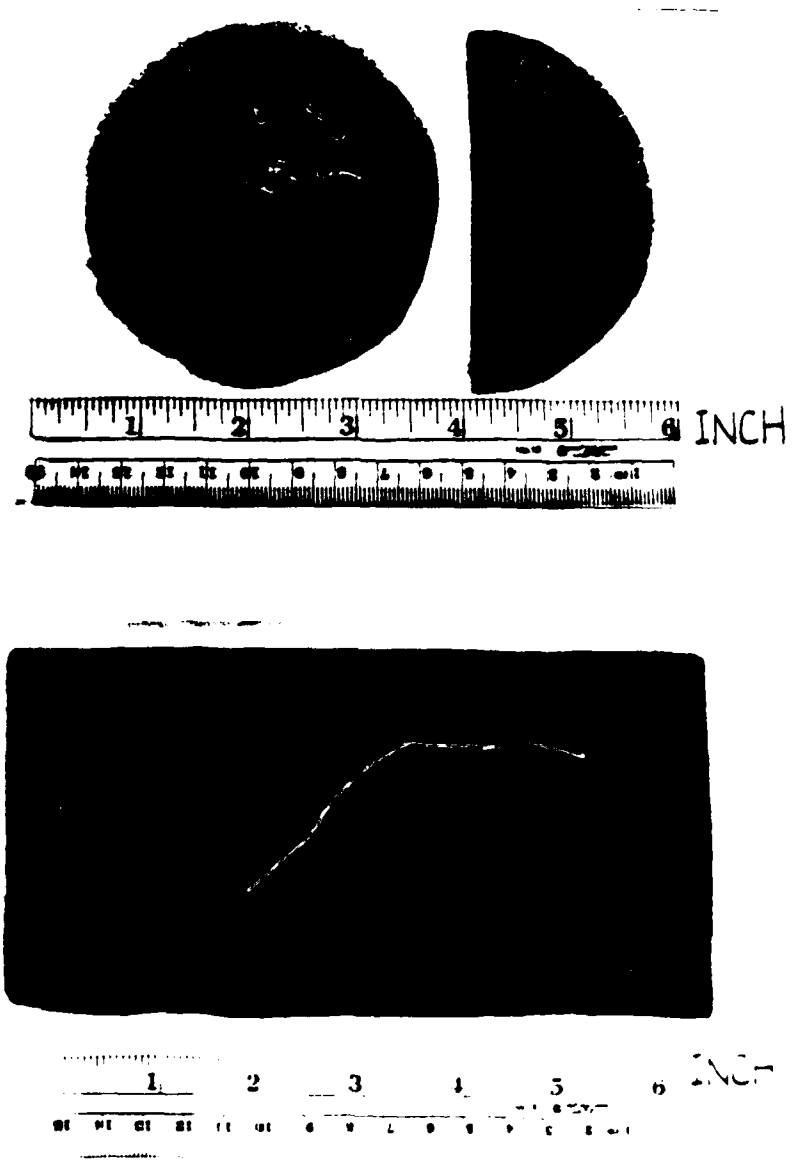


Figure 4a. Composite Preforms After Impregnation with Sol, Gel, Gelation, Drying and Pre-Heat Treatment; (a) Fiber Paper Reinforced, (b) Fiber-Mat Reinforced.

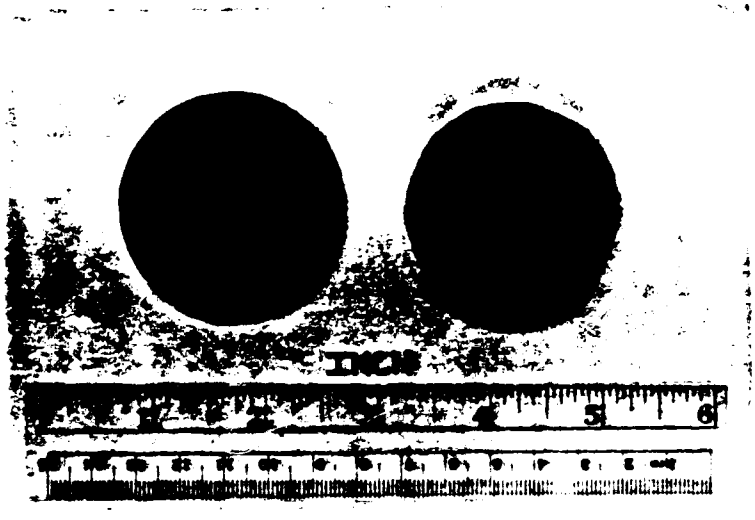


Figure 4b. Sol/Gel Composite Before (right) and After (left) Hot-Pressing.

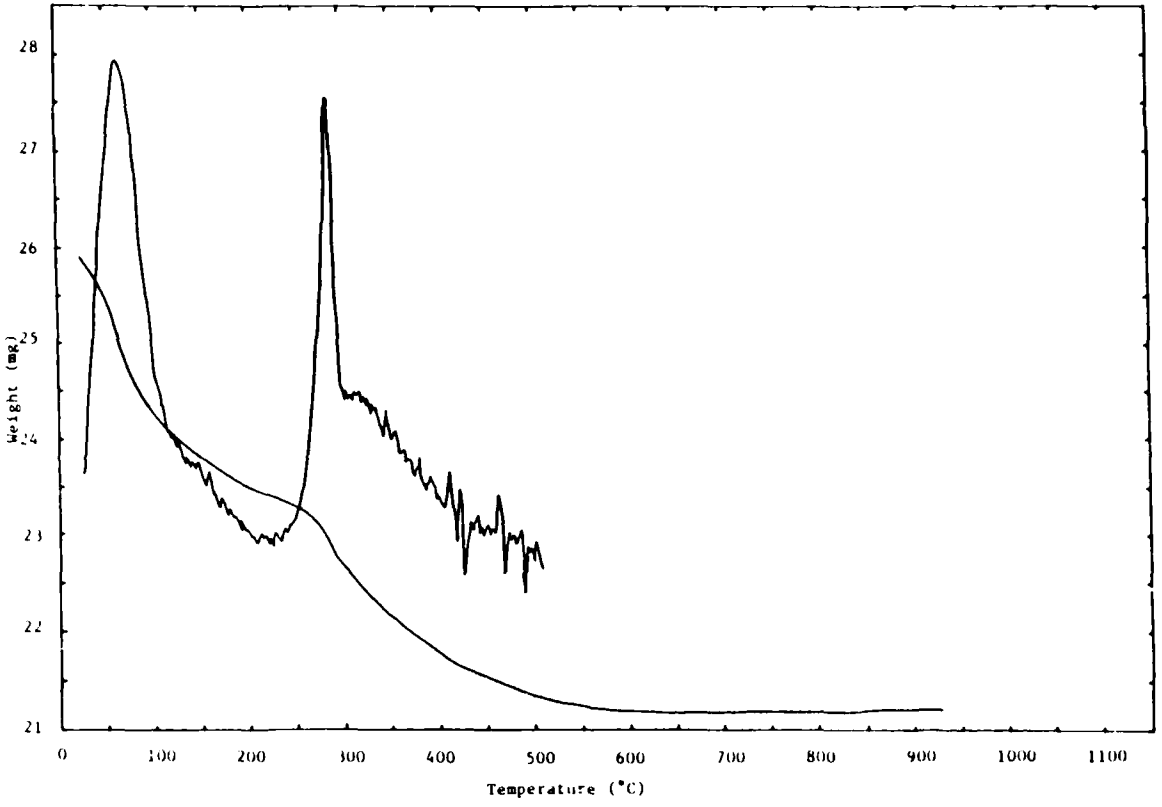


Figure 5. Thermogravimetric Analysis (TGA) of the Borosilicate Gel Matrix; The Weight Loss and Differential Weight Loss Curves.

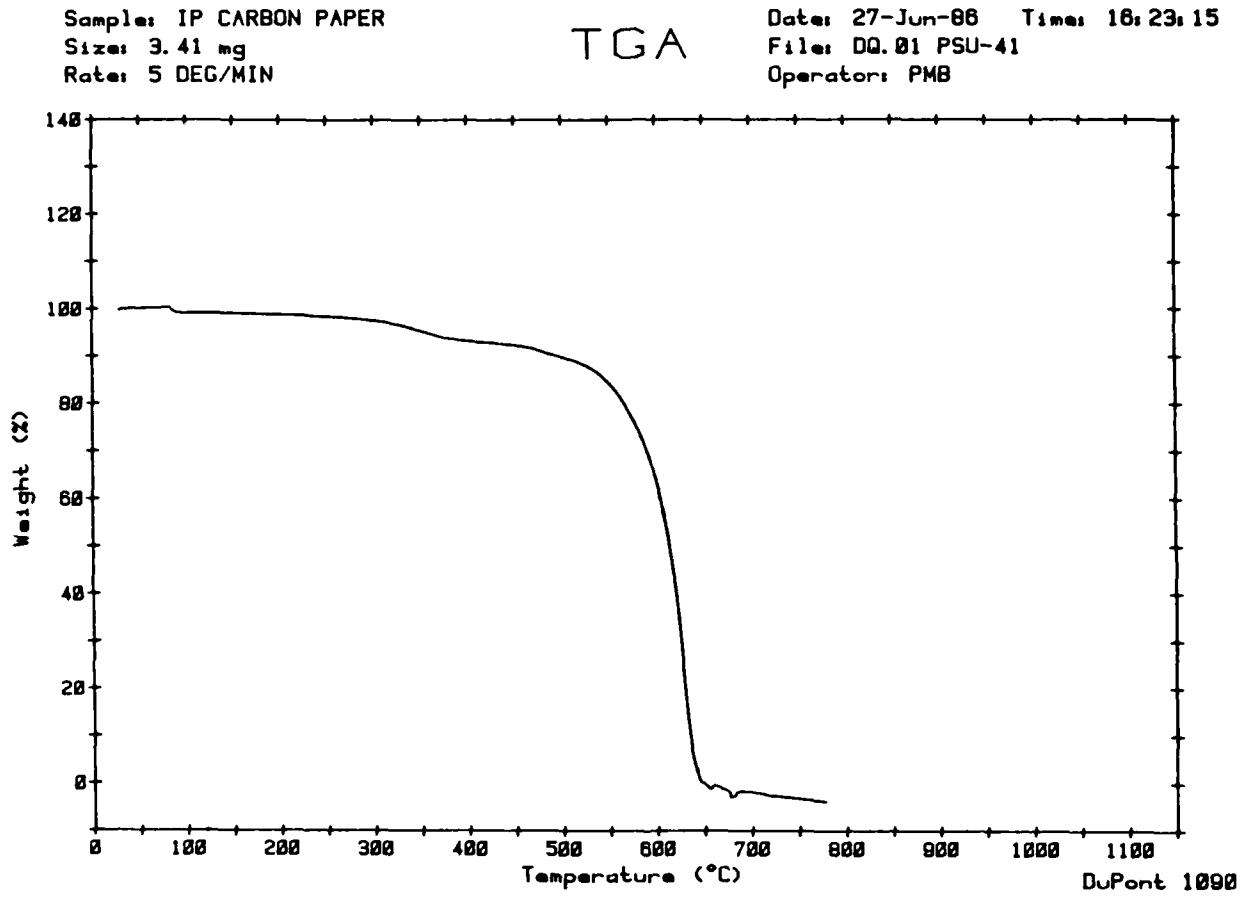


Figure 6. Thermogravimetric Analysis (TGA) of the Carbon Fiber Paper in Air.

One major concern with the heat treatment was the possible oxidation of the carbon fibers. Therefore, the heat treatment temperature and time must be carefully chosen. If the temperature is too low, or time too short, the residual organic matter could not be completely removed. Later, this would cause bloating of the composite during hot pressing. On the other hand, if the temperature was too high, the carbon fiber would be degraded. A variety of thermal analyses were used to establish the optimum heating schedule required to pretreat the gel matrix and composite.

Figure 5 shows a TGA trace of the borosilicate gel. The first weight loss peak around 70°C is associated with the desorption of water and alcohol in the gel. The sample lost about 9% of its original weight at this temperature. The second weight loss peak at ~280°C is due to the pyrolysis and carbonization of the residual organic groups; this contributes another 9% to the weight loss.

The TGA trace of the discontinuous carbon fiber paper is shown in Figure 6. It is apparent that in air, extensive oxidation of the carbon fiber occurs at around 625°C; i.e., the fiber was completely combusted at this temperature.. More important though, is the slow weight loss which begins at a much lower temperature. This may be due to the desorption of moisture and binder on the fibers, but could also indicate surface oxidation.

Some isothermal weight-loss analyses of the fiber, gel, and composite preforms were also carried out, but in this case, larger specimens were used in a furnace. The results indicated that the as-received bare fiber paper lost 7% of its weight after heating at 350°C for 30 min. In this case, it was believed that burn-out of the polyester binder was responsible. After increasing the heating time to 25 hrs, 12% weight loss was observed, and after heating 65 or 22.5 hrs, the total weight loss reached 18% and 30%, respectively. A prolonged heating for 64 hrs yielded 54% total weight loss. When the temperature was lowered to 300°C, it required about 4.5 hrs for the fiber paper to burn out its 7% organic binder (versus 30 min at 350°C). The borosilicate gel lost about 16% of its weight after heating at 285°C for 3.5 hrs, and after further heating at 350°C for 1 hr, this increased to 18%. No additional weight loss was observed even if the heating temperature was increased. In the case of the fiber reinforced gel preforms, longer times (or higher temperatures) were necessary to achieve weight losses comparable to those observed for the gel or fibers alone. The gel reinforced with 50 vol % of the fiber paper lost 11.30% of weight after 5 hrs of heating at 285°C. After further heating at 350°C for 1 hr, the overall weight reduction reached 12.68%. No further weight loss was observed.

The previously mentioned thermal analysis data led to the establishment of a heat treatment schedule for the composite preforms. The composite preform is heated to 100°C and held at this temperature overnight to remove physically adsorbed water and alcohol. The temperature is increased to 285°C and held for 5 hrs to allow for the pyrolysis of residual organics. Finally, the temperature is increased to 380°C and soaked for 0.5 hr to complete the process. The preform is then ready to be HP.

It should be mentioned here that many of the HP composites whose properties and microstructure as described in the following paragraph, were not heat-treated using this schedule. Early in the program, the heat-treatment was carried out at 350°C for 8-10 hrs due to the misconception that oxidation of the carbon fibers began only above 600°C. Therefore, it is likely that the fibers in many of these composites were partially oxidized and degraded.

Hot Pressing

Only the fiber-paper and fiber-mat reinforced composites had been hot pressed at the time of this report. The samples were hot pressed under vacuum using a graphite die. The hot pressing procedure was as follows:

1. the sample was placed in the graphite die,

2. the furnace system was evacuated,

3. the furnace was rapidly heated to 900°C-1000°C,

4. pressure was then applied (pressures in the range 1000-4000 lb/in^2 were evaluated),

5. the system was held at temperature and pressure for 20 to 30 min,

6. the pressure was released and then the furnace was cooled.

This schedule is subject to modification, since the analyses performed with these composites have shown that the temperature (when the pressure is released) may be important.

Mechanical and Thermal Properties

Only the flexural strength and thermal expansion coefficient of the composites were measured due to the limited size of these initial sets of HP specimens. For the three point bend test, the width, depth and test span of the specimen were 0.2, 0.2, and 1.9 cm, respectively. The crosshead speed was at 0.1 in/min. The test was performed at room temperature under two loading conditions: in one case, the fiber paper or mat ply was oriented normal to the direction of the applied load, and in the other case, the fiber ply was oriented parallel to the loading direction. Both polished and as-fabricated specimens were tested. For the thermal expansion measurements, the specimen employed was about 2 cm long with a 0.3 x 0.2 cm cross section. The thermal expansion was measured in the direction parallel to the fiber ply. A fused silica glass was used as a reference in the differential dilatometer and the measurement was conducted in air from room temperature to 400°C with a heating rate of 10°C/min.

Table 5 presents the flexural strengths of the hot-pressed sol/gel composites calculated from the three point bend test data using elastic beam theory. The strength of a conventionally melted Pyrex glass is also shown in Table 5 for comparison. The strength of the composites varied from 70 to 160 MPa which is far below the expected and desired value. The reason for this limited enhancement in composite strength over the matrix alone will be discussed in the section on Microstructural Characterization.

Figure 7 shows the thermal expansion behavior of 20 vol% fiber paper reinforced borosilicate glass matrix. Clearly, the composite contracted in the temperature range up to 90°C and then the composite began to expand at higher temperatures. After the system was cooled down, a second run was initiated. The thermal contraction was observed again, but the extent and temperature range for the contraction were reduced over the initial observation. After the third cycle, the initial thermal contraction was not observed. The low temperature contraction may be due to annealing effects and/or porosity in the composite. Additional studies will be necessary to determine whether this hysteresis is intrinsic to these materials or is due to their processing.

The CTE calculation based on the third cycle give an average thermal expansion coefficient of 15.6 x 10^{-7}/°C for the 20 vol % fiber paper reinforced composite and 12.0 x 10^{-7}/°C for the 40 vol % fiber reinforced composites for the temperature range of 25 to 400°C. These values are about one-half to one-third the thermal expansion coefficient of pure borosilicate glass which is about to 325 x 10^{-7}/°C. They are in good agreement with the value reported by Prewo (17 x 10^{-7}/°C) for a composite carbon fiber reinforced Pyrex composite, but one which was prepared by the conventional method (Ref. 20).

Table 5.

The Three Point Bend Strength of the Discontinuous Carbon Fiber Paper Reinforced Borosilicate Glass Matrix Composite

Vol % of Fiber	HP Temperature (°C)	HP Pressure (lb/in^2)	Flexural Strength (MPa) Load Normal to Fiber Ply	Load Parallel to Fiber Ply
8	900	1400	67	-
20	1000	4000	112	115
30	1000	4000	160	120
35	1000	4000	160	120
40	1000	4000	109	127
50	1000	4000	102	103

Note: The flexural strength of pure borosilicate glass is around 60 MPa

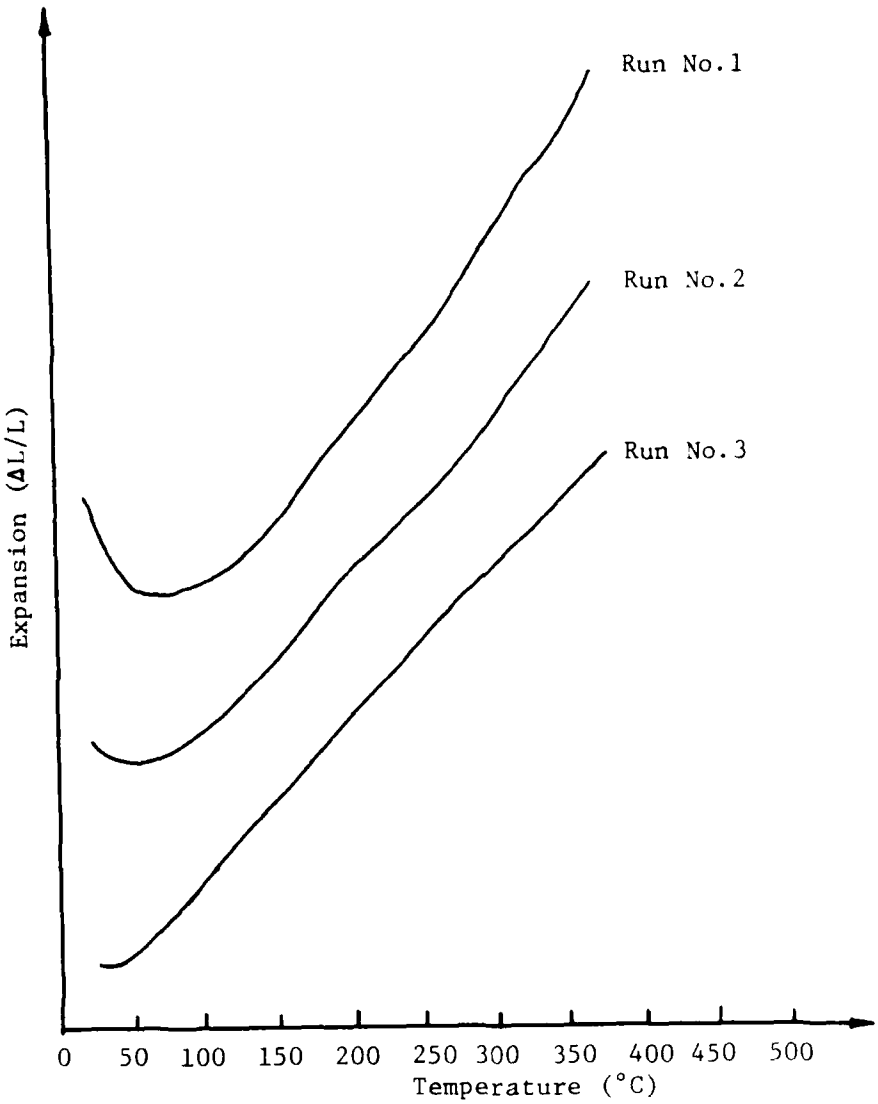


Figure 7. The thermal expansion behavior of the 20 vol % carbon fiber paper reinforced borosilicate glass matrix composite.

Microstructural Characterization

The microstructure of these composites was investigated by means of SEM and optical microscopy. Polished surfaces, as well as the fracture surfaces on the bend-bars, were examined. Figures 8 through 10 present some SEM micrographs of the HP composites. Three principal features should be noted: **(1)** the carbon fibers are indeed uniformly distributed within the glass matrix, **(2)** the fracture surfaces exhibit brittle characteristics rather than fiber pull-out which suggests strong-bonding at the interface, and **(3)** some local flaws and voids of the order 40 to 70 μm are observed. Clearly, points 2 and 3 are responsible for the low flexural strengths in these specimens.

IV. Discussion and Future Directions

In 1972, Sambell studied the reinforcement of borosilicate glasses with discontinuous carbon fiber (Ref. 14). He reported that the introduction of randomly-oriented discontinuous carbon fibers resulted in a decrease in strength. This strength decrease was more significant with increasing fiber fraction in the matrix. When the volume percent of fibers reached 40, it was found that the composite strength was reduced to 40% of the strength of the matrix alone. It was suggested that the randomly oriented discontinuous fibers weakened the composite by acting as stress concentrators in the brittle matrix. However, 10 years later Prewo (Ref. 7) reported that composites with flexural strengths in excess of 300 MPa could be achieved with discontinuous carbon fibers in a borosilicate glass matrix. The apparent discrepancy here is due to differences in the discontinuous fiber lengths. The average fiber length in Sambell's composites was shorter than 3 mm while the fiber length increased to ~19 mm in Prewo's study. According to Badkaree and Chyung (Ref. 34), the critical fiber length for the reinforcement of a glass matrix is between 3 and 6 mm. On this basis, the results obtained by Sambell and Prewo are not difficult to explain. Nevertheless, it should be mentioned that the limited amount of work on discontinuous fiber-reinforced glasses makes this conclusion somewhat tentative.

In this work, the average fiber length in the paper is ~25 mm (based on the information provided by the company) which is much longer than the critical length. Thus, it is somewhat unlikely that fiber-length is responsible for the low strengths observed. Rather, it is believed that strong interactions between the fibers and sol/gel matrix, and the presence of large voids, account for the low strength values. It has been recognized by many researchers that the degree of bonding between fiber and matrix determines, to a great extent, the strength and toughness of the fiber reinforced composite. Simply put, if the bonding is too strong, brittle failure occurs because cracks are not deflected at the fiber/matrix interface. In a strong and tough composite weak interfaces deflect the cracks and allow fiber pullout which is believed to be an important toughening mechanism.

The origin of the strong interfaces in these sol/gel composites is still unclear. It may be related, in part, to the presence of organic binders and coatings on the carbon fibers. These substances could interact with the alkoxides and solvents during the initial impregnation. Although one would expect these organics to decompose during subsequent heat-treatments, nevertheless, they may enhance or trigger interactions which would otherwise not be observed. It is also possible that the time-temperature schedule used in the hot-pressing is not optimized. Thus, there may be some interfacial oxidation due to extended time at temperature. This latter source of strong interfacial reaction would be further enhanced by the presence of volatiles in the matrix at the time of the HP. In any case, the composites now being fabricated utilize carbon fibers both with and without organic coatings to determine whether they influence the final properties.

It is also noteworthy that the Fortafil carbon paper in these composites utilize fibers with a peanut-shaped cross section (Figure 8). This characteristic influences the average fiber spacing which, in turn, can influence the strength. In fact, Prewo also noted a difference in the strength of composites fabricated with Fortafil (~200 MPa) versus other (~360 MPa) carbon fibers. This,

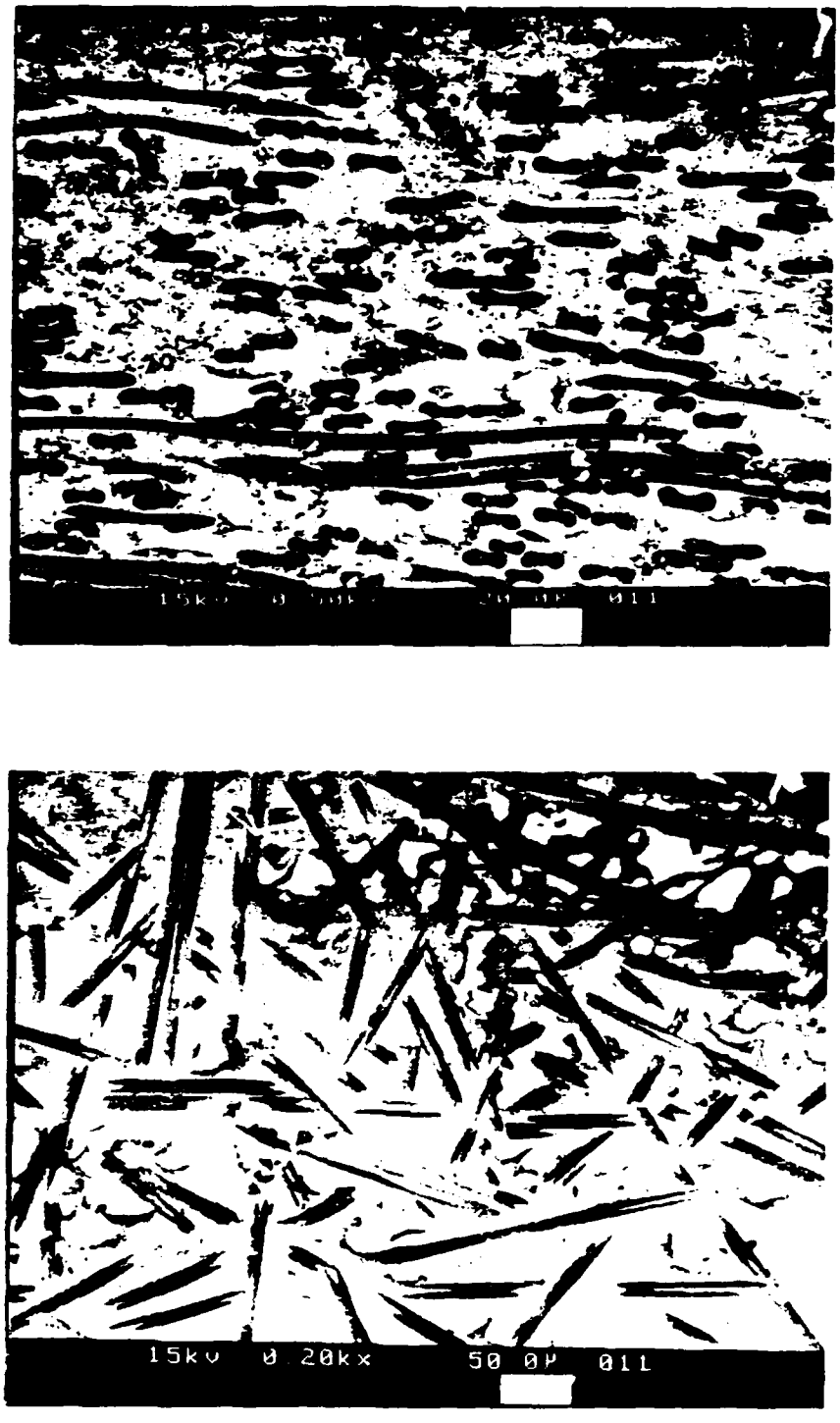
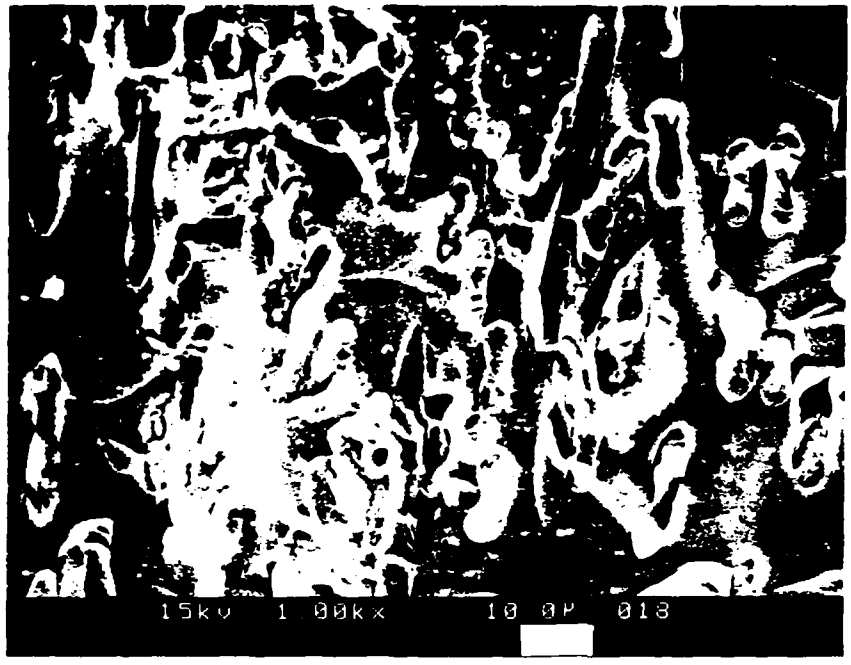


Figure 3. SEM Micrographs of the Polished Surfaces of Carbon Fiber-Paper Reinforced Composite; (a) Normal to Paper Ply, and (b) Parallel to Paper Ply.



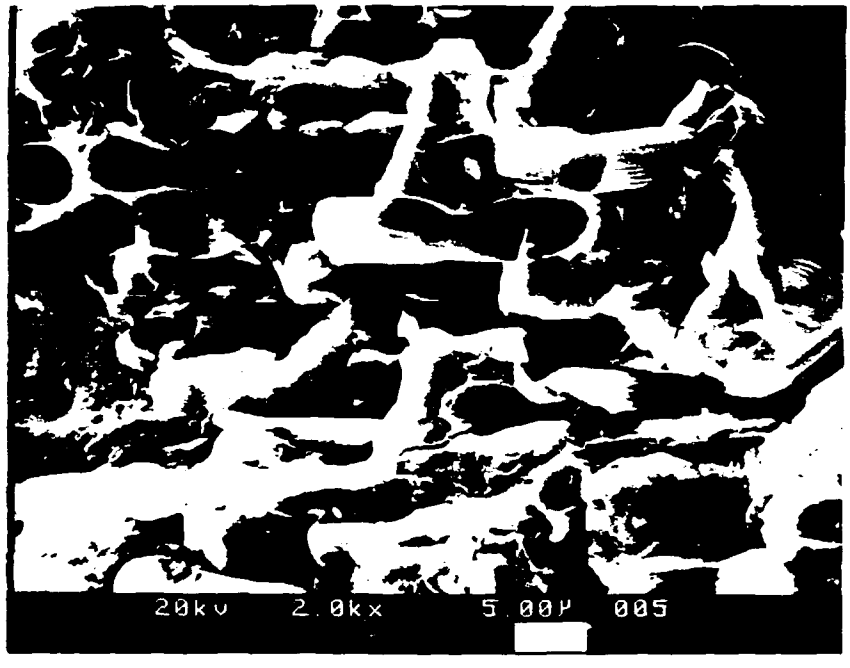
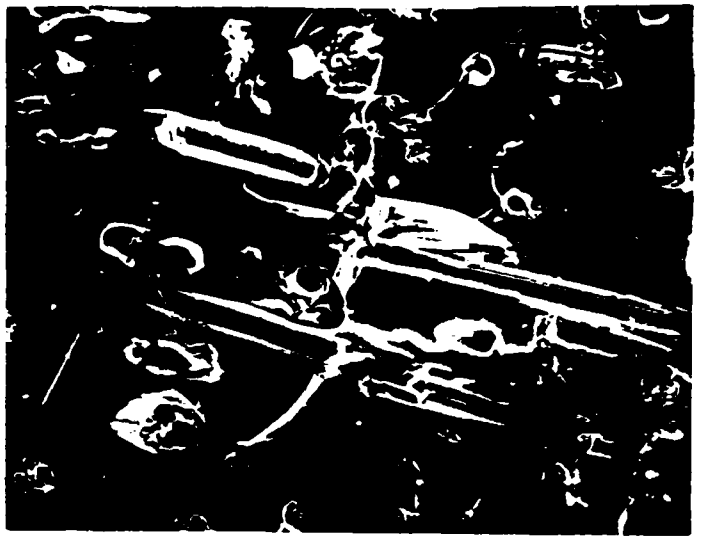


Figure 9a. SEM Micrographs of the Fracture Surface of the Fiber Paper Reinforced Composite; Note Brittle Failure Mode.



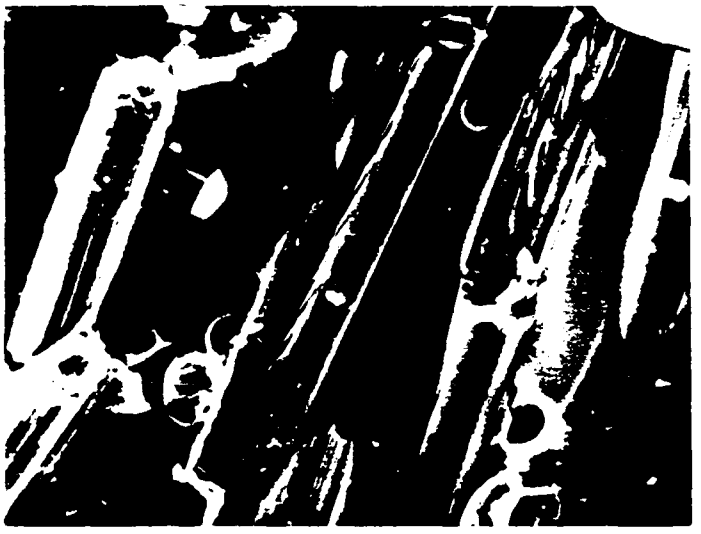
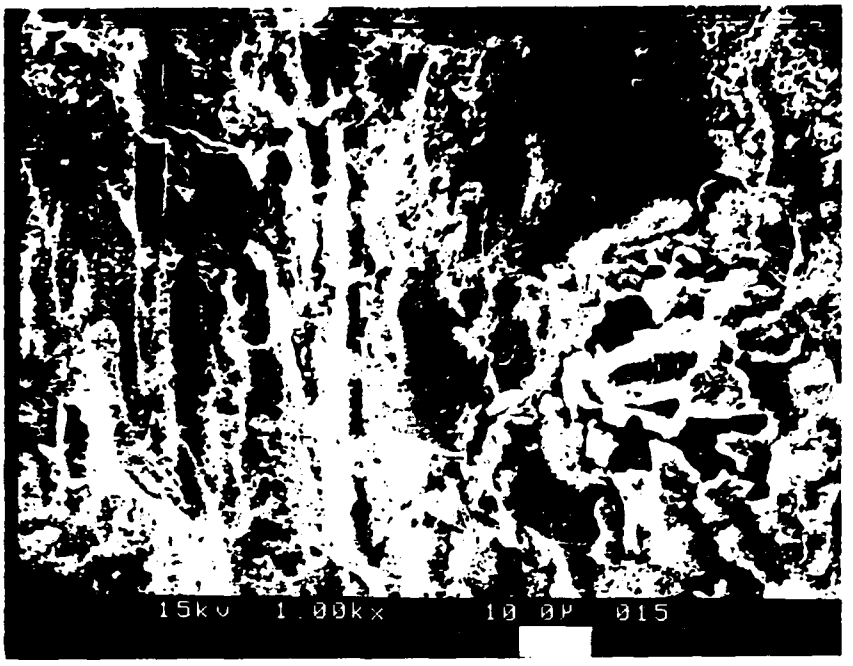


Figure 9b. SEM Micrographs of 'Pullout' in Selected Regions of the Fracture Surface; Note the Fiber-Surface Morphology and its Replication Within the Glass Matrix.



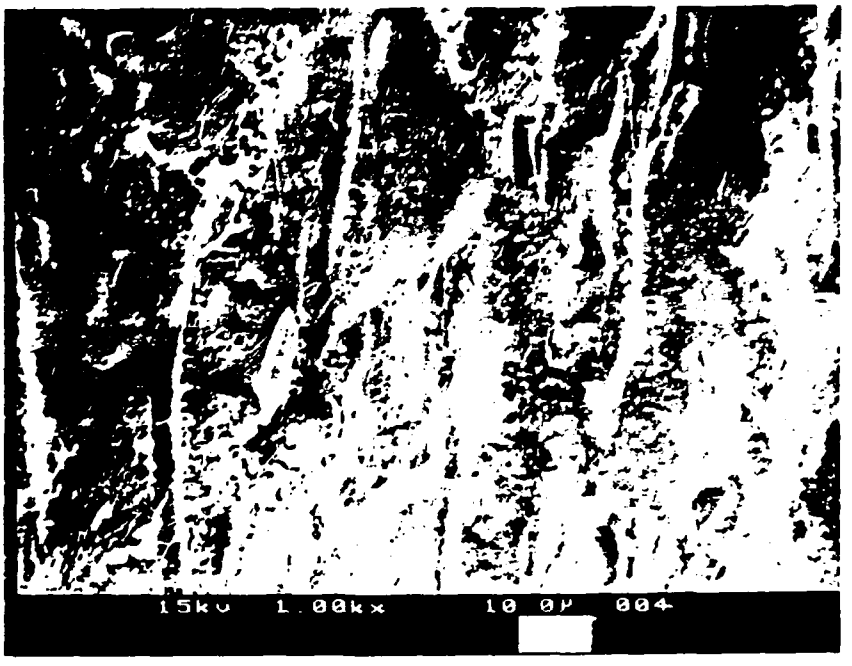


Figure [illegible]. SEM Micrographs which Show Residual Porosity and Large Flaws in Regions of the Fiber Paper Reinforced Composite.

too, may be influencing the strength of the composites reported herein. In the future, carbon paper whose fibers have a circular cross section will be utilized exclusively.

It was also suggested that existence of voids, porosity, and other defects may also contribute to the low strengths observed here. The data in Table 5 show little difference in strength for the edge-wise and flat-wise orientations. This is not to be expected, and thus, it suggests that the fibers (or fiber-paper plys) do not control the strength. There is no question that the origin of strength-controlling flaw lies in the processing, and clearly, we do not yet have sufficient experience in sol/gel processing of composites to address this issue in any detail. Nevertheless, one recognizes that **(1)** volatiles in the sol/gel matrix during HP, **(2)** oxidation during HP, **(3)** insufficient densification during HP, **(4)** less than optimal temperature-pressure conditions during HP, and **(5)** annealing conditions may all influence the defect levels in the composite. And the extent to which any one of these sources contribute to strength-degradation is further complicated by the volume fraction of fiber. That is, although an increase in fiber fraction should enhance the strength, the probability of defect generation during processing (due to the sources noted) will be greater at higher volume fractions. In this regard, the data in Table 5 also supports the contention that flaws control the strength in these samples, since there is no correlation between strength and fiber fraction.

Of course, one does not expect a composite of this sort to be sensitive to flaws or notches. Since the flaw insensitivity in these materials is usually attributed to crack-deflection, one concludes immediately that the interface characteristics are most detrimental to the strength; i.e., the interfaces render these particular sol/gel composites sensitive to flaws. Since the interface characteristics (as well as the defect generation) are primarily dependent upon the HP conditions, our future efforts must necessarily be focussed in this area. We have been working, to some degree, in collaboration with UTRC and their direction concerning the HP schedule will be of great benefit. Otherwise, the most important future direction is to process composites with these issues in mind. We now have established procedures for sol/gel synthesis of the glass matrix and for fabrication and heat-treatment of the preform. The challenge which remains is to optimize the HP densification step, and then, determine the extent to which the use of a sol/gel matrix precursor has influenced the final properties of the composite.

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