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COMPOSITE AND MICROCOMPOSITE FABRICATION VIA DEPLETION STABILIZATION ROUTES

by

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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GRADUATE STUDIES

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COMPOSITE AND MICROCOMPOSITE FABRICATION VIA DEPLETION STABILIZATION ROUTES

Abstract

by

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The colloidal phenomena of depletion stabilization and flocculation can be used to prepare high solids content slips with good fluidity. In this work these methods have been utilized as processing techniques to provide a controllable means by which monolayer and thicker coatings of matrix powder can be applied to fibers. External control of the particle-particle interactions dominating the stability of these slips reflects directly in the quality of the fiber coatings. As a result, ideal processing conditions for optimal coatings of fibers can be identified. Uniform coatings of up to 6 \( \mu \text{m} \) thick on AVCO SCS-6 fibers have been produced from slips of 0.07-0.3 \( \mu \text{m} \) diameter Si powder prepared using depletion strategies. The technique is effective even for asymmetric particle shapes (e.g. angular platelets) and wider size distributions. However, more uniform shapes and smaller size distributions were observed to result in dramatically improved, densely packed coatings.

Optimum processing conditions with maximum slurry solids loading and maximum particle-particle stability obtained using the depletion stabilization phenomena were scaled up for fiber weave infiltrations. Infiltrated weaves were cold and hot pressed and nitrided to enable evaluation of the infiltration quality via SEM
examination of cross sections of the infiltrated weaves. High quality Nicalon square and satin weave infiltrations were achieved using the depletion stabilization colloidal processing technique. Nitrided weave cross sectional samples showed a uniform infiltration of silicon powder throughout the matrix. A variety of additional weave styles and fiber types were infiltrated to determine the robustness of the technique. These weave styles were similarly uniformly infiltrated throughout.

An analysis was performed on the coating of a non-Newtonian fluid onto a vertical fiber surface continuously withdrawn from the fluid bath. The fiber coating thickness was determined to be a function of the fiber pulling speed, the fluid density and the parameters of the viscous model of the silicon slurry used. The analytic treatment also predicts the velocity profile of the fluid on the fiber surface in the region of constant coating thickness as a function of fiber pulling speed. The penetration of the slurry into a fiber bundle was also analyzed. The approximate penetration was estimated using the non-Newtonian fluid properties and fiber bundle parameters.
DEDICATION

This work is dedicated to my parents, Ann Dawn and Alexander Charles, for their loving support and encouragement through all these years; and to my husband, Mark Patrick, for his continuous inspiration, and his enthusiasm for my work. Thank you for helping me attain my goals. My gratitude and appreciation is always present.
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1.0 INTRODUCTION

Silicon based ceramics are potential replacements for strategic metals in applications ranging from heat engines to industrial heat exchangers because of their light weight, excellent oxidation resistance, high temperature strength and environmental stability. The primary drawback to their implementation is the difficulty in eliminating fracture generating flaws which can result in catastrophic component failure (Bhatt, 1985). In most cases, these flaws are introduced during the formation of the green compact and prior to sintering. The arrangement and packing density of particles in the green body determine the sintering behavior and the final properties of the ceramic. The flaws are commonly agglomerates which arise from the starting powder or the subsequent processing steps. A homogenous uniform product can only be obtained if the starting suspension has a high homogeneity and stability.

Reaction bonded ceramic matrix composites (CMC), such as reaction bonded silicon nitride (RBSN), offer the potential of improved, reliable high temperature properties. While shrinkage of the ceramic body occurs during conventional sintering, reaction bonded CMCs consolidate by filling the void space within the green part with reaction product. This allows the fabrication of near-net-shape bodies. Also, sintering aids are not required to relieve stresses resulting from particle/reinforcement arrangements. The absence of sintering aids in the grain
boundaries gives superior high temperature and corrosion properties. For reaction
bonded CMCs, processing temperatures are lower than those in conventional sintering
processes, however the sintering times are long. The use of silicon based materials is
severely limited because of their inherent flaw sensitivity and brittle behavior.
Reinforcement of these ceramics by high strength, high modulus continuous length
ceramic fibers should yield stronger and tougher materials.

1.1 Issues in Ceramic Powder Processing

Agglomerates, which are difficult to eliminate from dry powder consolidation
processes, control the flexural strength of sintered silicon-based ceramics. The strong
dependence of mechanical properties upon these flaws obscures the effect of other
variables such as composition, sintering time and temperature on the sintered
properties of silicon, silicon carbide and silicon nitride. One method that aims to
eliminate agglomeration is wet powder processing. Colloidal techniques can be used
to both improve the dispersion of the powder and control the flocculation of the
powder during consolidation into a uniform dense body.

Colloidal engineering strategies, which attempt to control the strength of the
interactions between solid particles when in their processing medium, have the
potential to provide an effective means to improve and control the green body
microstructure. One strategy to improve control during processing is to introduce
molecular additives to the system that will provide an externally adjustable colloidal
scale force. This induced force can be used to counteract and/or augment the inherent
van der Waals forces of attraction which is the cause of rapid agglomeration of
particles. In principal this can be achieved by one or a combination of two modes:
through electrostatic interaction where the necessary repulsive force is provided by a
double layer of ions and counterions surrounding the particles in suspension, or
through polymeric additives resulting in steric and/or depletion interactions.

1.2 Issues in CMC Processing

Fiber reinforced CMCs have the potential for high temperature structural
applications. However, the largest stresses in fiber reinforced CMCs, those
responsible for void and/or crack formation, occur primarily in the region close to the
reinforcing agent. Hence, the fiber-matrix interface plays a key role in the toughness
and failure mode of a composite. An effective and versatile method of modifying the
fiber-matrix interface is by coating the fibers and by fiber weave infiltration
techniques. In addition to providing the desired degree of bonding between the fiber
and matrix in order to optimize toughness, strength, creep and other properties, the
function of the coating on the reinforcing fiber may also be to protect the fiber during
handling and subsequent composite fabrication processes or in-service use (oxidation
protection or reaction barriers), and to provide compatibility with the matrix. Fracture
toughness and strength can only be realized if the fiber-matrix interface is able to
transfer the load from the matrix to the reinforcing fiber. A variety of techniques are currently commercially available for coating ceramic fibers with high-temperature materials, most commonly the techniques of chemical vapor deposition, thermal spraying and sol-gel coatings processes.

Woven fiber composites provide more balanced properties in the fabric plane than unidirectional fiber reinforced composites. The bi-directional reinforcement in a single layer of fabric results in excellent impact resistance. With multidirectional reinforcement isotropic mechanical properties can be approached. However the strength of weave reinforced composites is significantly lower than that of unidirectional fiber reinforced composites because only a fraction of the total fiber volume contributes to the strength in the testing direction. Depending on the intended end-use of the composites, these and several other factors dictate the choice of the type of reinforcing agent. Hence, both the coating of unidirectional fibers and the infiltration of fiber weaves are subjects of this study.

In the fabrication of ceramic-fiber reinforced composites, the uniformity of infiltration by the matrix powder into the fiber layups or throughout the fiber tows or weaves is of additional concern. Inhomogenous powder packing can result in nonuniform densification upon sintering, and the subsequent degradation of mechanical properties and reliability of the final ceramic. Furthermore, problems associated with nonuniform densification rates can lead to warpage, microcracks and
lack of dimensional control in finished components. Many of the heterogeneities in
the powder such as agglomerates, inclusions and voids, can in principle be eliminated
from the starting powders by manipulating and controlling interparticle forces.

1.3 Colloidal Engineering Strategies: Depletion Routes

Depending on whether polymer additives adsorb onto the solid surface or
remain freely in solution, different types of control can be realized (Napper, 1983).
Steric stabilizers are those polymers that adsorb onto the surface of the solids. If
solution conditions are favorable, steric stabilizers provide a repulsive interaction
between approaching particles, and hence can effectively prevent flocculation.
Depletion stabilizers refer to those polymers that do not adsorb to any large extent
onto the ceramic solids.

This research investigates the use of the colloidal phenomena of depletion
stabilization/flocculation to enhance the processing of ceramic composites and
microcomposites. The depletion stabilization technique has several advantages over
steric stabilization strategies for controlling the interaction of submicron scale solids
and hence may be especially useful for CMC processing. Since only very low
molecular weight steric stabilizers are used in conjunction with the depletion
stabilizers, there is a minimal addition of organic matter to the ceramic solids. This
should translate to higher green density and better uniformity of surface coverage of
the fibers. Secondly, high solids content slips having high fluidity can be prepared. Finally, polymer additives used to control the stability are not attached to the ceramic solids. These additives are automatically excluded from the green composites and can be recovered for economy of reuse. In steric stabilization, all of the steric stabilizing material must be burned out as part of the densification schedule.

1.4 Outline Of Dissertation

This work investigates the application of the depletion stabilization/flocculation phenomena as a route for enhanced ceramic processing. There are three major goals for this research: (1) demonstration that the depletion effect could be used to control the stability and loading of silicon slips; (2) the use of silicon slips prepared at optimal depletion conditions to prepare ceramic composites and microcomposites; and (3) modeling of some of the processing phenomena for use in the analysis of process scale up.

The first goal was to demonstrate the depletion effects in silicon slips. To accomplish this goal, several tasks had to be undertaken. These included the identification of proper additives for both the depletion stabilizer and the steric stabilizer for the silicon particles. In this work, polystyrene was added as the depletion additive, and C_{18} chains were used as the steric stabilizer. The C_{18} chains were grafted to the surface of the silicon particles via a pseudo-esterification reaction.
A variety of tests were applied to the C₁₈ grafted silicon particles to verify the quality of the organic coating. These included measurement of the particle size distribution of the solids dispersed in organic and aqueous media as well as adsorption isotherms for the polystyrene. Phase separation experiments were performed to identify the critical concentration of polystyrene that induces the depletion effect. Measurements of the rheological characteristics of the phase-separated suspensions were performed to characterize the stability of these slips. Measurement of the sediment volume was used to quantify the solids loadings in the phase separated slips.

The second goal was to utilize slips prepared at optimal concentrations for the preparation of particle-coated single silicon carbide fibers and as infiltrant into weaves of silicon carbide powders. Particle-coated fibers were prepared by manually dipping short lengths of fibers into the phase-separated slips prepared under different degrees of depletion stabilization. Electron microscopy was used to ascertain the quality and density of the particle coatings on the fibers. The quality of the coating was found to correlate with the effectiveness of depletion stabilization. The effects of multiple dipping of the fibers was also studied. Infiltration experiments were performed by multiply dipping small samples of woven ceramic fibers into slips prepared at optimal depletion conditions. These materials were further processed and nitrided. Following sectioning of these composites, electron microscopy was used to investigate the quality and uniformity of the infiltration.
Modeling was the final goal of this work. The coating of a non-Newtonian fluid onto a vertical fiber surface continuously withdrawn from a fluid bath was also analyzed. The fiber coating thickness and velocity profile was determined as a function of the fiber pulling speed, the fluid density and the viscous model of the fluid. Upper limits on the coating thicknesses were established. Finally the penetration of a silicon/cyclohexane slurry into a fiber bundle was modeled in terms of the capillary action driving the infiltration and the viscous resistance to the fluid motion.

Prior to this work, depletion stabilization/flocculation effects have not been demonstrated on colloidal ceramic silicon particles. The effects of the depletion stabilization phenomena have previously been experimentally studied only for ideal sol-gel silica systems with controlled particle growth via the Stoer process (Stoer, 1968) resulting in highly spherical silica particles with uniform particle size. The particles are grown via a system of chemical reactions by means of hydrolysis of alkyl silicates and subsequent condensation of silicic acid in alcohol solutions. These systems contrast to the milled, angular shaped primary ceramic silicon particles with wide size distributions such as the primary particles used in this work.
2.1 Colloidal Engineering Strategies for Processing Ceramics

The fabrication of ceramic components from submicron sized powders is a useful approach to obtain reproducible and reliable products. Processing powders in the submicron size range however requires good control over particle-particle interactions. Good control over particle-particle interactions in dry powder consolidation is difficult to achieve since spontaneous agglomeration of the powder may occur as a result of the intrinsic van der Waals force of attraction and the presence of static charge on the powders (Freedman, 1986). In general, the wet consolidation of a ceramic slip provides a more controllable route over particle-particle interactions.

A ceramic slip or dispersion is a colloidal suspension of a fine powder in a processing medium. In this work the processing medium is nonaqueous. The colloidal stability of solid-liquid dispersions with respect to agglomeration depends on the sign and magnitude of the total energy of interaction between particles. The general equation for describing the total potential of interaction between a pair of suspended particles, $V_T$, incorporates the sum of attractive and repulsive contributions: the electromagnetic effects which lead to London-van der Waals attraction, $V_A$; the particle surface charge effects and the interaction of the double
layer. $V_{DL}$ and: steric and other polymeric stabilization mechanisms of interaction.

$V_R$. Assuming these contributions to be additive (Moreno. 1992):

$$V_T = V_A + V_{DL} + V_R$$  (1)

The attractive contribution is always present due to the tendency of the particles to be in contact with each other by means of London-van der Waals forces. The attractive contribution can to some extent be manipulated through the use of solvent additives or by chemical modification of the solid surface. Electrostatic repulsion is the result of the development of a charged electrical double layer around each particle, built up by dissociation of surface groups or adsorption and reaction of potential determining ions from solution, upon dispersing a powder into a polar liquid. The repulsive force produced decreases with increasing separation between the particles. The magnitude of this repulsion can be controlled externally by varying the ionic strength of the processing media, by changing the number of surface sites that can acquire charge, or by masking the surface with surfactants or polyelectrolytes. Electrostatic repulsion is less effective in nonaqueous media than in water because of the lower ionic concentration and lower dielectric constant of nonaqueous liquids.

Polymeric stabilization may be achieved by two different mechanisms: steric stabilization where the macromolecules are attached to the particle surface, and: depletion stabilization in which the macromolecules are free in solution. The polymeric stabilization mechanism of steric repulsion confers stability through the physical interaction of long-chain polymers or other surfactants adsorbed onto the solid surface. Steric stabilization is as effective in nonaqueous media as in aqueous
media. The overall stability of the suspension is achieved when the repulsive forces are high enough to dominate over the attractive London-van der Waals forces.

2.2 Depletion Stabilization/Flocculation Theory

There are two different mechanisms whereby polymer chains can impart colloidal stability: steric stabilization and depletion stabilization. Steric stabilization of colloidal particles is imparted by macromolecules that are attached by chemical grafting or by physical adsorption to the surface of the particles. There have been many reviews of steric stabilization showing the rapid improvement in understanding in recent years. The understanding of the mechanism of steric stabilization however is not as advanced as electrostatic stabilization.

Depletion stabilization differs from steric stabilization in that stability is imparted not by attached polymers but by macromolecules that are free in solution. This phenomena was first studied experimentally in 1975 (Li-in-on, 1975) and theoretically in 1980 (Feigin, 1980). Investigations of this phenomena are however still in their infancy.

It is possible to have combinations of electrostatic and steric stabilization which has been called electrosteric stabilization. The electrostatic component originates from a net charge on a particle surface such as through an attached
polyelectrolyte. It is also possible to have a combination of depletion stabilization with steric stabilization as in this work, or combinations of depletion stabilization with both steric and electrostatic stabilization.

Figure 1 shows a suspension of ceramic solids in a polymer solution. The polymer is chosen so that it does not significantly adsorb onto the solid. The ceramic solids are unaffected by the presence of the dissolved free polymer below a minimum polymer concentration. The free polymer adopts an equilibrium coil configuration that depends on solution conditions. At higher polymer concentrations, there will be adequate polymer to be distributed throughout the solids. As two solid particles approach, the equilibrium coil configuration of a free polymer molecule between them is distorted. The polymer molecule has the tendency to return to its equilibrium configuration, providing a stabilizing action towards any further approach of the particles. A minimum amount of polymer is necessary to provide an adequate "depletion stabilization". The minimum concentration of polymer required to provide adequate depletion stabilization is referred to in this work as the limiting concentration and denoted as $C_{lim}$.

A particle immersed in a polymer solution experiences an osmotic pressure acting normal to its surface. For an isolated particle, the integral of the pressure on
Figure 1:  Pictorial representation of depletion effects.
the entire surface nets zero force. But when the depletion layers of two particles overlap, polymer will be excluded from the portion of the interparticle gap. Consequently the pressure due to the polymer solution becomes unbalanced, resulting in an attraction. Such a situation occurs above a higher critical free polymer concentration. Above this higher critical free polymer concentration, the number of free polymer molecules per unit volume of fluid that can exist in the gaps between the solid particles is lower than that in free solution. This induces an osmotic pressure difference between the interparticle gaps and the free solution. As a result, the solvent is driven from these regions, thereby inducing the particles to approach even closer. As the particles are induced to approach under the osmotic pressure difference, clusters of particles begin to form as solvent continues to be depleted. Through gravity and the difference in density between the particle clusters and the expelled solvent, a phase separation occurs. Ultimately the initially homogenous slip separates into two distinct phases. Under gravity, the lower phase contains virtually all the solids, while the upper phase contains most of the free polymer. Due to the continued depletion of solvent into the upper free polymer rich layer, the solids in the upper phase will agglomerate as the particles are driven together, resulting in "depletion flocculation". The concentration of polymer required to initiate phase separation is denoted herein as \( C_{pl} \). The graph in figure 2a qualitatively illustrates the effect of increasing free polymer concentration on the depletion stabilization and flocculation forces between the particles.
The above brief description of the depletion phenomena describes the idealized case of bare particles and free non-adsorbing polymer. However, all ceramic solids will adsorb polymer to some degree, thereby preventing the polymer from remaining completely free in solution. We can ensure that the polymer does not significantly adsorb onto the solid by providing a thin coating on the ceramic powder that will yield a barrier to adsorption of the free polymer. As a result, at high free polymer concentrations when the particles are forced together as the solvent is driven out from the interparticle gap by the osmotic pressure difference, the thin coatings on the particles begin to overlap. The particle coatings begin to act as steric stabilizers and there is a counterbalancing osmotic pressure build up in the fluid that prevents the particles from excluding all of the solvent from between the particle surfaces. Ultimately the dispersion will still separate into two distinct phases. During this process most of the dissolved polymer is excluded from the region occupied by solids. The lower phase contains all of the solids stably dispersed in the processing fluid and very little of the free polymer. The volume of the lower phase is small so that the solids loading in this phase is high. The upper phase contains most of the free polymer.

The combined depletion and steric effects described above are graphically represented in figure 2. Figure 2a shows the effect of increasing polymer.
Figure 2: Qualitative representation of the effect of increasing free polymer concentration on interparticle force and dispersion stability.
concentration on the interparticle force for bare particles effected by the depletion phenomena. At low polymer concentration, \( C < C_{ps} \), the suspension remains a single phase fluid with the particles uniformly dispersed. Above the phase separation concentration \( C_{ps} \) the system separates into a dense particle rich lower phase in equilibrium with the polymer solution upper phase. \( C_{mn} \) representing the minimum free polymer concentration required for depletion stabilization to occur, and \( C_{ps} \) denoting the free polymer concentration required to induce the phase separation are indicated on the graph. Figure 2b shows the constant interparticle repulsion resulting from a thin steric coating applied to the particle surfaces to prevent the free polymer from adsorbing. The repulsive steric effect is unaffected by increasing free polymer concentration. Figure 2c shows the net effect of polymer concentration on interparticle potential when the two phenomena are combined. \( C_r \) represents the polymer concentration at which the depletion flocculation forces overcome the steric repulsion forces and a net flocculation results. At any concentration above \( C_r \) the lower phase is flocced. The phenomena has been reported to occur with silica particles dispersed in cyclohexane and toluene containing polystyrene free polymer at theta conditions (de Hek, 1981) and for particles stabilized by grafted polymer chains in solutions of the same or different polymer (Cowell 1978, Vincent 1980, Clark 1981, Vincent 1986). In this work the operating conditions for optimum fiber coating and fiber weave infiltration occur when \( C_{ps} < C < C_r \). Operating in this concentration range allows us to take advantage of both the high solids loading resulting from the phase separation and the maximum slurry stability resulting from the balance of the
interparticle forces.

There is a limit to the amount of counterstabilizing action that can be generated by the organic surface group on the powder for a given system. As the concentration of free polymer is increased, the forces of depletion flocculation become stronger than the maximum steric stabilization force provided by the organic barrier. Under these conditions, instabilities will be introduced into the system, although a phase separation is still induced.

The coating on the particle fulfills several functions in this processing strategy. The organic coating prevents the bare ceramic powder from adsorbing polymer. Additionally, by providing a steric barrier, the coating allows us to utilize the high volume concentration resulting from the phase separation due to the depletion flocculation phenomena. The final advantage is specific to our system. As will be described later, we have chosen silicon powder as our ceramic solid and cyclohexane as our processing media. Silicon powder, with unavoidably oxidized surface silanol groups, agglomerates in organic cyclohexane. However if a sufficient number of hydrocarbon groups are bonded to available silanol surface sites, the powder will become more organophilic and less hydrophilic, thereby allowing us to continue processing in organic cyclohexane media.
In addition to its concentration, the magnitude of the stabilizing action provided by the depletion polymer can be controlled by several other externally adjustable factors. Manipulating the system temperature can be used to favorably alter the interactions between the solids in the system. Usually the temperature is chosen so that the depletion stabilizing polymer is near its theta temperature for the processing medium. Raising the system temperature further away from the theta temperature will result in a larger tendency to solvate the polymer and draw more solvent from between the particles. This can lead to binding of the solids to each other. It is also possible to utilize the solution thermodynamics of the grafted steric stabilizers. If the proper steric stabilizer can be chosen, and the system temperature dropped to below the theta temperature of these polymers, binding would also occur.

The distance of approach of the solids at which the stabilizing action arises depends directly on the radius of gyration of the polymer in solution. The radius of gyration is determined by the molecular weight of the polymer as well as the solvency of the fluid medium. As is the case with steric stabilization approaches to control particle interactions, the solvency of the fluid medium can be altered by varying the system temperature or by blending nonsolvents into the processing medium.
2.3 Surface Chemistry of Silicon

The surface of any clean silicon substrate is oxidized rapidly at room temperature to at least a monolayer of silicon by exposure to oxygen or water vapor or the ambient environment (Mizuta, 1982). The oxidation rate and the ultimate structure of the silica layer is dependent both on the oxidation conditions and the structure/composition of the original substrate. For dry and wet oxidation of silicon the assumed passive oxidation reactions respectively are (Hess, 1990):

\[
\text{Si}_{(s)} + \text{O}_{(g)} \rightarrow \text{SiO}_{2(s)} \tag{2}
\]

\[
\text{Si}_{(s)} + 2\text{H}_{2}\text{O}_{(g)} \rightarrow \text{SiO}_{2(s)} + 2\text{H}_{2}\text{O}_{(g)} \tag{3}
\]

Both reactions follow a parabolic rate law which for long times reduces to (Hess, 1990):

\[
x^2 \cong B \times t \tag{4}
\]

where \(x\) is the thickness of the oxide layer, \(t\) is the time elapsed and \(B\) is the coefficient containing the effective diffusivity and interfacial concentration of the oxidizing species.

Since a clean silicon surface rapidly oxidizes at room temperature, the chemistry of the surface layer of silica greatly influences the colloidal behavior of the system studied in this work. Surfaces of silica undergo varying degrees of hydration. The surface species of silica are generally classified as free silanols, hydrogen-bonded
adjacent silanols or siloxanes.

\[ \begin{array}{ccc}
\text{H-O} & \text{O-H} & \text{O-H} \\
\text{Si} & \text{Si} & \text{Si} \\
\text{Free surface silanol} & \text{Hydrogen bonded surface silanol (vicinal)} & \text{Siloxane}
\end{array} \]

The siloxanes represent a low degree of hydration of the surface silica, while the vicinal silanol surface corresponds to a high degree of hydration. Silanol groups are strongly hydrogen bonding and therefore are hydrophilic and interact favorably with polar fluids. Due to steric effects, isolated free silanols can interact to a different extent with polar fluids than can vicinal molecules. On the other hand, the siloxanes do not hydrogen bond, making them hydrophobic. Thus the relative amounts of siloxanes and silanols determine the degree to which silicon powder interacts with the dispersing media. Powder with a high surface silanol population will be readily wetted by aqueous media, while a large siloxane group population leads to easy wetting by non-polar media. A fully hydrated silica surface containing no siloxanes has approximately 4.5 Si-OH surface sites/nm\(^2\) (Armstead, 1969). Of the 4.5 surface silanol sites/nm\(^2\), 3.2 sites/nm\(^2\) are hydrogen bonded and 1.3 sites/nm\(^2\) are free silanols. The number of surface sites varies depending on the particular structure and commercial source. Baking a silica surface in an inert environment at 1000°C for 24 hours completely dehydrates a silica surface (Iler, 1979).
2.4 Fibers

A fiber by definition is a thread-like structure having a length at least 100 times its diameter. Fibers can be definite short lengths (non-continuous) or continuous. The principal driving force for the development of new ceramic fibers was the need for high temperature reinforcing fibers for aerospace applications. A wide range of both continuous and non-continuous ceramic fibers are available including oxide, nitride and carbide composition, fiberglass and graphite fibers.

Carbide fibers prepared by pyrolysis of polymers or by chemical vapor deposition processes (CVD) are a class of ceramic fibers with significantly different properties from those of oxides. Silicon carbide fibers are available commercially in both continuous and non-continuous (whisker) forms. Silicon carbide fibers in continuous form may be described as monolithic or bi-component types. The monolithic type includes Nicalon (Nippon Carbon Co. Ltd.) silicon carbide fibers. Bicomponent silicon carbide fibers prepared by chemical vapor deposition of silicon carbide on a carbon core are available from AVCO Specialty Materials division, Textron Co., Lowell, Massachusetts. These bi-component fibers have significantly higher strengths and modulus of elasticity than continuous silicon carbide fibers produced by polymer pyrolysis. Improved AVCO fibers comprise of a protective CVD carbon silicon coating called “SCS” consisting of carbon enriched with silicon
The principal advantage of carbide fibers over available oxide fibers is the superior mechanical properties which have been or are potentially obtainable, especially higher modulus of elasticity. Carbide and nitride fibers are also relatively resistant to reaction with matrices such as glasses, metals or other ceramics for reinforced composites. Because of its mechanical properties, silicon carbide is a promising candidate for reinforcing applications. Silicon carbide also offers the advantages of low cost, high heat resistance (up to 1200°C), low electrical conductivity, corrosion resistance/chemical stability, wettability for metals and compatibility in plastics.

2.4.1 Fibers for Ceramic Matrix Composites

The key criterion for selecting fibers for structural ceramic matrix composites is the thermomechanical stability in an oxidizing environment during processing and in end uses. DiCarlo (DiCarlo, 1984) suggests the ideal fiber qualifications for strong and tough ceramic matrix composites are: a continuous fiber, high length/diameter ratio, small diameter, high strength, high strength retention in oxygen and in other hostile environments, creep resistance, and thermal expansion near that of the matrix. Several high-performance continuous fibers are becoming available which meet the demand for low density (<4000 kg/m³), high Young's moduli (>200 GPa), and high
tensile strength (>2 GPa). At the 1200° to 1300°C range, SiC and Si₃N₄ fibers are promising. SiC multifilaments (such as Nicalon fibers) and monofilaments (such as the SCS series) are presently of particular interest. Nicalon fiber is known for its ability to be woven into textile structures. SCS fibers are renowned for their thermal stability. However because of the large filament diameter (140µm) the processability of SCS fibers into textile structures is limited.

Fiber architecture can be classified into four categories: discrete, continuous, planar interlaced (two dimensional), and fully integrated (three dimensional) structures (Ko. 1989). Discrete fiber systems such as whiskers have no material continuity. The orientation of the fibers is uncontrolled and the structural integrity of the preform comes mainly from interfiber friction. The second category of fiber architecture is the unidirectional (0°) continuous filament system. This architecture has a high level of continuity and linearity and is suitable for angle-ply tape layup structures. However the lack of in-plane and out-of-plane yarn interlacings result in intralaminar and interlaminar weakness. The third category of fiber reinforcement is the planar interlaced and interlooped system. The intralaminar planar is corrected with this system, but the interlaminar strength is limited by the matrix strength due to the lack of through thickness fiber reinforcement. In the fully integrated system, the fourth category of fiber architecture, the fibers are oriented in various in-plane and out-of-plane directions. With continuous yarn filaments a three dimensional network
of yarn bundles forms an integrated structure resulting in additional reinforcement in the through-thickness direction. As a result, the composite is virtually delamination free. These three-dimensional woven, knit and braided cloths can assume complex structural shapes.

Yarns composed of spun discrete fibers are called staple yarns. Yarns having continuous fibers are continuous filament yarns. Most high-performance yarns are continuous filament yarns having single (such as the SCS series) or multiple (such as Nicalon) strands. A fabric is defined as an integrated fibrous structure produced by fiber entanglement or yarn interlacing, interloping, intertwining or multiaxial placement. Weaving, knitting and braiding can produce planar or three-dimensional structures. The two- and three-dimensional fabrics are distinguished by yarn orientation distribution and the number of yarn diameters in the thickness direction. A two dimensional fabric consists of two or three yarn diameters in the thickness direction with fibers oriented in the x-y plane. Three-dimensional fabrics consist of three or more yarn diameters in the thickness direction with fibers oriented in all three directions.

All woven fabrics consist of two sets of interlaced threads, known as warp and fill threads. The types of fabrics can be identified by the pattern of repeat of the interlaced regions. Two basic geometrical parameters can be defined to characterize a fabric: \( n_f \) denotes that a warp thread is interlaced with every \( n_f \)th fill thread and \( n_w \)
denotes that a fill thread is interlaced with every \( n_{wq} \)th warp thread (Ishikawa 1982). Figure 3 schematically illustrates the warp and fill threads that identify a pattern of repeat units. Fabrics with \( n_{fg} = n_{wg} = n_g \) and \( n_g \geq 4 \) and where the interlaced regions are not connected are known as satin weaves. As defined by their \( n_g \) values, the fabrics are termed plain weave (\( n_g = 2 \)), twill weave (\( n_g = 3 \)), 4 harness satin (\( n_g = 4 \)) and 8-harness satin (\( n_g = 8 \)).

Hundreds of possible woven fabric combinations are made by interlacing yarns. From the point of view of in-plane fiber orientation, woven fabrics can be divided into biaxial and triaxial woven structures. Biaxial weaves consist of 0° and 90° yarns interlaced in various repeating patterns. The three basic weave geometries from which many other patterns evolve are the plane, satin and twill weave as defined above and shown in the schematic diagram in figure 4. These three fabrics are distinguished by their frequency of yarn interlacing and the linearity of the yarn segments. The plane weave has the highest frequency of yarn interlacing, the satin weave has the least number of yarn interlacing and the twill weave is in between. As a result the plain weave has the highest level of structural integrity and greater ductility. However the satin weave has the highest level of fiber-to-fabric strength, a higher fiber packing density and a higher fiber-volume fraction.
Figure 3: Schematic representation of warp and fill threads that identify a pattern of repeating units.
Figure 4: Structural geometry of a) plain ($n_y=2$), b) twill ($n_y=3$) and c) satin ($n_y=4, 8$) weaves.
3.0 EXPERIMENTAL

3.1 Surface Preparation of Silicon Powder

3.1.1 Procedure

The silicon powder used was high purity Union Carbide (lot# 50054) powder with a range of particle size between 1-20 µm. The impurity content of the as-received powder as reported by the manufacturer is shown in table 1 below. This powder contained a high volume fraction of large particles (≥ 20µm) which are larger than the interfiber distance in the desired composites. To reduce the particle size and to promote reactivity during nitridation, the as-received silicon powder was attrition milled in a Si₃N₄ container with Si₃N₄ balls and cyclohexane for 24-72 hours depending on the particle size desired. The chemical analysis, average surface area and particle size of the powder before and after attrition milling for 24 hours are shown in table 2. From the table it can be seen that milling for 24 hours results in a significant increase in the oxygen, carbon and nitrogen content. Carbon picked up is associated with the cyclohexane used as the milling fluid. Oxygen and nitrogen were picked up from air exposure during and after milling. The surface area of the powder increased from 1 m²/g to 16 m²/g while the average particle size decreased from 10 µm to 0.785 µm. Particle size analyses were obtained using a Microtrac Particle Size
Analyzer (Leeds and Northrup Company, Largo, Fl.). The BET (N₂ adsorption) specific surface area was determined using a Quantasorb Jr. Sorption System (Quantachrome Corp., Syosset, NY). After milling, the excess solvent was evaporated from the powder. The powder was dried and stored under a vacuum until the next stage of processing.

Table 1: Trace impurity analysis of as-received Union Carbide silicon powder

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
<th>Al</th>
<th>Ca</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Ti</th>
<th>V</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.17</td>
<td>0.02</td>
<td>0.08</td>
<td>0.53</td>
<td>0.08</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 2: Chemical analysis, surface area, and average particle size of silicon powder

<table>
<thead>
<tr>
<th>material</th>
<th>O wt%</th>
<th>C wt%</th>
<th>N wt%</th>
<th>Fe wt%</th>
<th>BET m²/g</th>
<th>size µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-rec Si</td>
<td>0.43</td>
<td>0.025</td>
<td>0.004</td>
<td>0.6</td>
<td>1.6</td>
<td>10</td>
</tr>
<tr>
<td>24hr milled</td>
<td>1.2</td>
<td>0.31</td>
<td>0.07</td>
<td>0.6</td>
<td>16.7</td>
<td>0.785</td>
</tr>
</tbody>
</table>

Cyclohexane was chosen as the processing medium for all remaining processing stages due to its usefulness in demonstrating the depletion phenomena with silica solids in previous work (Pathmammanoharan 1981, de Hek 1979, 1981). The thin steric barrier was provided by grafting 1-octadecanol (Aldrich Chemical Company) to the silicon powder. Monodisperse polystyrene (Pressure Chemical Company) with molecular weight 5780 was used as the depletion stabilization additive. Small amounts of ethanol aided in the dispersion of the silicon powder and in dissolving the 1-octadecanol. The silicon powder coatings were applied to AVCO SCS-6 silicon carbide fibers.

Isolated free and vicinal silanol groups on the surface of the silicon powder are
strongly hydrogen bonding, and therefore interact favorably with polar groups. The silicon powder was rendered lyophilic by taking advantage of the surface silanol groups, resulting from inevitable oxidation, as sites for the grafting of 1-octadecanol. The grafting proceeds via a two step reaction. In the first step shown in equation 5, the activation step, the isolated free and vicinal silanol surface groups are dehydrated to siloxane groups. Adsorbed water is removed in the condensation of adjacent silanols to form reactive surface siloxane species. In the second step, a pseudo esterification reaction, the surface siloxane groups react with alcohols (1-octadecanol in this work) to form alkoxides as shown in equation 6. For the purpose of the reaction it is not important what material comprises the interior of the particles reacted. Esterification occurs rapidly at 150-200°C.

$$\equiv \text{Si} - \text{OH} + \equiv \text{Si} - \text{OH} \rightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{H}_2\text{O} \quad (5)$$

$$\equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{C}_{18}\text{H}_{37} - \text{OH} \rightarrow \equiv \text{Si} - \text{O} - \text{C}_{18}\text{H}_{37} + \equiv \text{Si} - \text{OH} \quad (6)$$

The resulting particles are covered with a layer of aliphatic chains thick enough to prevent the polystyrene from adsorbing yet still thin enough (~2nm) to have negligible effect in later processing/burn out. For the purposes of the reaction it is not important what material comprises the interior of the particle. However at least two layers deep of SiO₂ are required on the silicon particle surface for the esterification
reaction so that the topochemical properties of the substrate are essentially those of pure SiO₂. Despite the presence of at least two SiO₂ layers, even in the most complete esterification reaction the number of ester groups/nm² never exceeds the equivalent of one monolayer. Figure 5 is a diagrammatic representation of a portion of a particle with an esterified surface. Silaceous solids have numerous pores, voids and interstices. Exposed surfaces existing in the interior of the particle may be connected to the exterior. Hence liquid and gases can penetrate the pores and reach exposed surfaces of pores walls. The esterification of surface silanol groups on the silicon powder is described by Iler and coworkers (Iler, 1956) for primary and secondary alcohols. Ballard and coworkers (Ballard, 1961) showed that the degree of esterification increases with reaction time and temperature.

The degree of C₁₈H₃₇ coverage and the uniformity of coverage is affected by the primary particle size and shape, pore size and distribution, amount of water in the system which may block possible reaction sites if not removed, the packing of the siloxane units and degree of initial oxidation, reaction temperature and reaction time. The extent of coverage in turn affects the degree of organophilic and hydrophobic properties of the esterified product. A certain minimum number of ester groups per unit surface area makes the products organophilic. As this number is increased, the preference for organic solvents increases. At a much higher concentration than the minimum, the products are not only highly organophilic but they can cease to be hydrophilic, i.e., they are hydrophobic and organophilic. Some uncovered surface
area can be present provided that the repulsion of water by the surface ester groups is greater than the attraction of water by the uncovered areas. According to Iler (Iler, 1953), to render a surface siliceous material markedly organophilic it is necessary to have present on the surface more than 100 ester groups/100 nm$^2$ of substrate surface area. A hydrophobic surface requires more than 200 ester groups/100 nm$^2$ of substrate surface. Even when a reaction product is rendered hydrophobic with a minimum number of required ester groups, the surface is not completely crowded with ester groups and still may have some exposed surface silanol groups. Products with maximum stability towards hydrolysis have ester groups crowded so closely on the surface that the surface is completely protected. This requires more than 270 ester groups/100 nm$^2$ for most ester groups. The internal structure of the silicon substrate is unaffected by esterification.

The 1-octadecanol grafted particles reacted as described above were easily dispersible in organic solvents such as cyclohexane. The grafted C$_{18}$H$_{37}$ layer provided an effective barrier to the depletion polymer to prevent particle surface adsorption. The presence of the C$_{18}$H$_{37}$ layer also provided stability in the high solids loading lower phase that resulted from the phase separation process. The method of the surface grafting esterification reaction did not additionally increase the overall
Figure 5: Diagrammatic representation of a particle with an esterified surface.
oxidation of the powder. hence does not adversely affect the nitridation reaction occurring in later processing.

The reaction above was performed as part of a multistep procedure. After milling in cyclohexane and drying the silicon powder, the powder was then redispersed in ethanol and ultrasonically pulsed (Heat Systems Inc., Farmingdale, NY) to break up any agglomerates that may have been formed. Since no generation of gaseous products was observed as a result of the dispersion of silicon in ethanol, we expected that the surface of the silicon powder was at least partially oxidized prior to dispersion.

A concentrated solution of 1-octadecanol in anhydrous ethanol was added to the suspension of silicon in ethanol so that the weight of 1-octadecanol was three to five times the weight of silicon powder. Following the evaporation of all the ethanol by heating, the temperature was raised to 200°C and held for three to six hours depending on the degree of esterification desired, while the esterification reaction occurred. Continuous stirring and a constant flow through of ultra high purity N₂ at 7 ft³/hr ensured that any water present as a byproduct of the reaction was removed, thereby avoiding blockage of possible reaction sites. Before entering the reactor, the ultra high purity N₂ gas (minimum purity 99.999%, O₂ 1 ppm maximum) flowed through an oxygen scavenger to reduce the oxygen level to less than 0.1 ppm. The flow through of N₂ additionally provided an inert atmosphere and prevented any
further oxidation of the surface of the silicon powder. Figure 6 is a schematic
diagram of the esterification reaction apparatus. The large excess of 1-octadecanol
was used so that silicon interparticle contacts were minimized to prevent irreversible
siloxane-bridge formation in the intermediate reaction stage. Such irreversible
aggregations by siloxane-bridge formation between different particles has been
reported in the literature (Iller, 1979). For this reason it was also important to keep the
water concentration as low as possible just before the esterification reaction, because
siloxane-bridge formation is retarded in a nonaqueous medium.

Following the reaction time the system was cooled and the excess unreacted 1-
octadecanol was removed by a combination of vacuum distillation (160 mTorr,
180 °C) with N₂ flow (0.5 ft³/hr) and sedimentation. N₂ gas was blown over the 1-
octadecanol melt containing the silicon powder. The 1-octadecanol vapor was carried
by the N₂ along the reactor to a cold section where the vapor crystallized. This
method is severe enough to remove all excess 1-octadecanol but not severe enough to
damage the chemically bound 1-octadecanol. The tubular reactor used for removal of
excess 1-octadecanol is shown in figure 7. The dry solid Si-C₁₁₈H₁₇₇O powder was
then redispersed into a 60/40 mixture of chloroform and cyclohexane. Chloroform is
a good solvent for 1-octadecanol. Cyclohexane was added to increase the density
difference of particle and medium, hence decreasing the centrifuge time required for
Figure 6:  Schematic diagram of esterification reaction apparatus.
PHASE 2: REMOVAL OF EXCESS 1-OCTADECANOL

Figure 7: Schematic diagram of tubular reactor used for removal of excess 1-octadecanol.
the silicon powder to sediment and remove any physically adsorbed $\text{C}_{18}\text{H}_{37}\text{OH}$. The remaining coated silicon powder was stored suspended in the cyclohexane until used in further processing stages. $\text{C}_{18}\text{H}_{37}\text{O}$ bonded silica powder prepared by an analogous procedure has been stored for up to two years without significant degradation of the organophilic character (Van Helden, 1981).

The separation of the $\text{C}_{18}\text{H}_{37}\text{O}$-silicon powder from the large excess of 1-octadecanol can be achieved by sedimentation alone or by vacuum distillation alone. Separation of the powder dispersed in excess 1-octadecanol/chloroform/cyclohexane requires an ultracentrifuge due to the high density of the liquid resulting from the large amounts of 1-octadecanol present. Separation via this technique was time intensive and laborious because of the long centrifuge times and the repeated washings required to remove all the excess 1-octadecanol. The ultracentrifuge operated under refrigeration as a safety measure to prevent potential explosions from occurring with volatile solvents in the environment of the elevated temperatures generated by the centrifuge during operation. Additionally the cool temperatures required for operation of an ultracentrifuge resulted in the 1-octadecanol solidifying and precipitating out before the silicon powder has sedimented. When using vacuum distillation alone to remove the 1-octadecanol it was difficult to exactly determine when all the 1-octadecanol was removed. Prolonged vacuum distillation after all the 1-octadecanol was removed appeared to result in aggregation of the silicon particles. Hence the combination of vacuum distillation and sedimentation was the most
effective and efficient technique. The surface of the esterified silicon takes on the characteristics of the esterifying alcohols: the powder is rendered organophilic and hydrophobic. The effectiveness of the chemically bonded organic groups on the silicon surface after combined vacuum distillation/sedimentation was evaluated both qualitatively by visual examination and quantitatively in terms of particle size distribution, electron microscopy images and polymer adsorption studies.

3.1.2 Results and Discussion

A scanning electron microscope was used to examine both the bare silicon after 24 hours of milling and C_{18}H_{37}O attached silicon after 2 hours of esterification reaction time. The SEM micrographs of the bare and C_{18}H_{37}O-silicon powder particles are shown in figure 8 at a magnification of \( \times 15,000 \). The process of esterification did not appear to have any significant effect on the particle size or shape. The micrographs also indicated that any agglomerates formed during storage were broken up before the onset of esterification resulting in only primary particles participating in the esterification reaction.

After 72 hours of milling the as-received powder, the bare silicon powder agglomerated and rapidly sedimented immediately when dispersed in cyclohexane. In
Figure 8: SEM micrographs of 24 hour milled powder showing (a) unreacted silicon surface before esterification and (b) reacted silicon surface after 2 hr esterification reaction time.
ethanol the bare silicon dispersed well and required several hours before the onset of obvious sedimentation. In contrast, after 2 hours of esterification reaction time the silicon with attached C<sub>18</sub>H<sub>37</sub>O groups rapidly agglomerated in ethanol while it appeared visually to be well dispersed in cyclohexane. These qualitative observations suggested that the C<sub>18</sub>H<sub>37</sub>O surface groups were effective in rendering the silicon powder organophilic and hydrophobic after a minimum of 2 hours reaction time at 180-200°C.

A particle size analysis was performed on four suspensions of 72 hour milled silicon powder: silicon in ethanol, silicon in toluene, silicon-C<sub>18</sub>H<sub>37</sub>O in toluene and silicon-C<sub>18</sub>H<sub>37</sub>O in ethanol. All samples were subjected to pulsed 20 kHz ultrasonication (Model W-225 Ultrasonic Processor, Heat Systems, Inc., Farmingdale, New York) for approximately 60 seconds prior to beginning the particle size analysis.

A combination of sedigraph (Model 5000E, Micromeritics Instrument Corporation, Norcross, Georgia) and Nicomp Submicron Particle Sizer (model 370, Santa Barbara, California) particle size analyzers were used to obtain particle size distributions over the range of 0.01-50μm. The mean particle sizes determined respectively for these suspensions are shown in table 3.

<table>
<thead>
<tr>
<th>Suspension</th>
<th>Mean Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon in ethanol</td>
<td>0.13</td>
</tr>
<tr>
<td>silicon in toluene</td>
<td>8.49</td>
</tr>
<tr>
<td>silicon-C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;37&lt;/sub&gt;O in toluene</td>
<td>0.36</td>
</tr>
<tr>
<td>silicon-C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;37&lt;/sub&gt;O in ethanol</td>
<td>21.8</td>
</tr>
</tbody>
</table>
These results show that the presence of the C_{18}H_{37}O groups on the surface of the silicon renders the powder organophilic and hydrophobic after a minimum of 2 hours reaction time at 180-200°C.

The most important role of the C_{18}H_{37}O group on the surface of the silicon particles is to provide a barrier to prevent free polystyrene from adsorbing onto the particle surface. Isotherms for the adsorption of polystyrene onto silicon were measured. A variety of experimental techniques are available to measure adsorption isotherms at a solid-liquid interface. In this work the change in polymer concentration was measured in terms of differences in the refractive indices of the pure solvent and the polymer solution using a differential refractometer (Model RF-600, CN Wood Mfg Co., Newtown, Pa.). The experimental apparatus and technique is described in detail elsewhere (Kerkar, 1991). The concentration range studied was between 0-5 wt% of polystyrene. The solvent used was a cyclohexane/toluene blend (86.9/13.1). The cyclohexane/toluene blend was used because of the lower theta temperature of the blend compared to the higher theta temperature of pure cyclohexane. The temperature of the differential cell was maintained at 30°C, significantly above the theta temperature of polystyrene in cyclohexane/toluene of 15°C. Each solution/solvent pair was allowed to thermally equilibrate within the cell for 10 minutes. Suspensions of 5 wt% silicon in cyclohexane/toluene were ultrasonically dispersed, then equilibrated by agitation in sealed tubes using a test tube shaker (Lab
Industries, Berkeley Ca.) for 24 hours at a constant room temperature of 22°C which
was above the theta temperature for polystyrene in the solvent blend. The solvents
used in preparing the suspensions were the same as those used to calibrate the
differential refractometer. The samples were centrifuged and the supernatant
analyzed for polystyrene concentration using the differential refractometer. The
adsorption isotherms for polystyrene onto bare silicon and silicon-C\textsubscript{18}H\textsubscript{37}O from
cyclohexane/toluene are shown in figure 9.

The bare silicon powder adsorbed significantly larger amounts of polystyrene
in comparison to the silicon-C\textsubscript{18}H\textsubscript{37}O, although both showed relatively low
adsorbances. The adsorption of polystyrene onto the silicon surface is influenced by
several factors, most importantly by polymer-medium interactions. Solubility
parameters, $\delta$ (cal/cm$^3$)$^{0.5}$, provide an approximate way of quantifying the
interactions. The closer the $\delta$ of the medium to that of the polymer, the better the
solvency for the polymer. Since the solubility parameters for polystyrene (8.56),
cyclohexane (8.2) and toluene (8.9) are close to each other, the polystyrene will
predominantly remain in the solvent. As a result we observe relatively low adsorption
isotherms for both the bare silicon and coated silicon cases.

Adsorption of polymers is also influenced by the relative competition between
the polymer and medium to occupy silicon surface sites. This depends on the
Figure 9: Adsorption isotherms for polystyrene onto bare silicon and silicon-C_{18}H_{37}O in cyclohexane/toluene (86:9:13:1) solvent
chemical nature of the species involved. The cyclohexane/toluene medium (non-polar) competes with the polystyrene in adsorbing onto the silicon-\(\text{C}_{18}\text{H}_{37}\text{O}\) organic surface or oxidized SiO\(_2\) surface in the case of bare silicon. Since the silicon-\(\text{C}_{18}\text{H}_{37}\text{O}\) is better dispersed than the bare silicon in the cyclohexane/toluene medium, we expect less polystyrene adsorption and lower adsorption isotherms. Hence the lower adsorption exhibited by silicon-\(\text{C}_{18}\text{H}_{37}\text{O}\) implies it is a good candidate for depletion stabilization which utilizes non-adsorbing polymers.

Because of the broad particle size distribution (0.07 - 0.3\(\mu\)m) and the expected thin size of the protective \(\text{C}_{18}\text{H}_{37}\text{O}\) barrier, it is difficult to experimentally determine the thickness of the barrier. Theoretically it can be estimated from C-C interatomic bond lengths that the \(\text{C}_{18}\text{H}_{37}\text{O}\) barrier is a maximum of 2.6 nm thick. This represents approximately 5.5 wt\% for an average 0.115 \(\mu\)m particle, assuming all surface sites were grafted.

Thermal Gravimetric Analysis, TGA, (TGA7, Perkin Elmer, Norwalk, CT) was used to determine the degree of \(\text{C}_{18}\text{H}_{37}\text{O}\) coverage on the silicon surface as a function of esterification reaction time. In all TGA studies the temperature was ramped at a rate of 100\(^\circ\)C/min from an initial temperature of 35\(^\circ\)C to a final temperature of 500\(^\circ\)C under a N\(_2\) atmosphere maintained by a N\(_2\) flow rate of 60 cc/min. A range of from 2 to 5.4 wt\% weight loss occurred depending on the length
of esterification reaction time, indicating the degree of $C_{18}H_{37}O$ coverage. After only 2 hours reaction time TGA showed ~ 1.5 wt % $C_{18}H_{37}O$ present. After being ultrasonically pulsed for 2 minutes, these powders dispersed well initially but began to sediment in 20 minutes. Up to 4.5 wt% $C_{18}H_{37}O$ coverage can be achieved by 6 hour reaction times. After ultrasonic pulsing these powders remained well dispersed for several days without the formation of any appreciable sediment.

TGA of powder samples was also used to determine the effectiveness of the chloroform/cyclohexane washing after vacuum distillation removal of the excess 1-octadecanol. TGA of Si-$C_{18}H_{37}O$ reacted and unwashed powder indicated 7.7% weight loss. In dispersion studies these powders remained well dispersed for up to 2 weeks without appreciable sediment formation. After the same powder was subjected to chloroform/cyclohexane washing and centrifuging, TGA showed 3.7% weight loss. The resulting powder remained well dispersed for 48 hours before the onset of sedimentation. Because the TGA showed that weight loss occurring at lower temperatures (350°C at atmospheric pressure) was absent in the washed powders, the 3.7 wt% difference is attributed to physically adsorbed $C_{18}H_{37}O$ present. The additional physiosorbed $C_{18}H_{37}O$ explained the extended dispersion times before onset of sedimentation. Chloroform/cyclohexane washing appears to be effective in removing any $C_{18}H_{37}O$ present.
3.2 Phase Separation

3.2.1 Procedure

Concentrated dispersions of silicon-$C_{18}H_{37}O$ esterified powder in cyclohexane were obtained via phase separations resulting from the depletion stabilization/flocculation phenomena. By changing external parameters (polystyrene concentration in this work) which governed the depletion forces, the degree of stability of the slips resulting from phase separation was varied, which in turn was reflected in the quality of the silicon coatings on the dipped SCS-6 fibers. Varying concentrations of polystyrene in cyclohexane were prepared by pipetting stock solutions of polystyrene with pure cyclohexane into test tubes. A constant mass of silicon-$C_{18}H_{37}O$ was added to the tubes (5 wt%). The tubes were tightly stoppered to prevent evaporation of the cyclohexane, and the dispersions thoroughly mixed. The tubes were allowed to stand in a water bath at 40°C and periodically observed for up to 72 hours.

Within an hour two phases separated by a sharp interface could be distinguished between a clear upper phase believed to be rich in polystyrene and a dark, silicon rich lower phase. Up to 8 hours were allowed to ensure completeness of the phase separation. The clear upper phase was removed via a pipette. AVCO SCS-6 fibers cut into approximately 2-3 cm lengths were then dipped into the silicon rich
lower phase. After allowing the cyclohexane to evaporate and the coatings to dry, the silicon powder coated fibers were examined with an electron microscope.

3.2.2 Results and Discussion

Phase separations similar to those described by Pathmamanoharan and coworkers (Pathmamanoharan, 1981) and de Hek and Vrij (de Hek 1979, 1981) were observed. After combining silicon powder with polystyrene and cyclohexane and thoroughly mixing, tubes with a polystyrene concentration greater than the phase separation concentration, $C_{ps}$, became turbid. Within one hour two liquid phases separated by a sharp, visible interface could be distinguished. Within four hours the separation was complete and the volume of the lower phase remained unchanged. The interface between the phases was fluid reflecting the expected low viscosity of the lower phase. On gently shaking the tubes, the two phases easily became one turbid phase again, which reseparated into two phases after standing in the water bath at $40^\circ$C for several hours, indicating the reversible nature of the depletion phenomena.

The lower phases contained approximately 18 volume percent (approximately 40 wt%) silicon solids. Tubes with polystyrene concentration less than $C_{ps}$ showed no phase separation after mixing and standing at $40^\circ$C for up to 24 hours, when a gravity sediment slowly began to form. A reference tube for comparison was also prepared with each set of experiments in which only silicon and cyclohexane were present. In these reference tubes gravity settling was the only mechanism responsible for the slow
formation over time of a lower phase. The photograph in figure 10 shows four tubes prepared at different polystyrene concentrations: on the far left is the reference tube containing no polystyrene, next is a tube prepared with a polystyrene concentration less than the phase separation concentration \( C_{ps} \), the third tube was prepared at \( C_{ps} < C < C_r \), and the fourth tube was prepared at a concentration greater than \( C_r \), the concentration at which the onset of flocculation occurs.

The location of the phase separation concentration \( C_{ps} \) varied depending on the differences in silicon particle size distributions between batches. Smaller size distributions resulting in larger average surface area/gram required larger amounts of depletion polymer to achieve phase separation. The length of esterification reaction time also affected the location of \( C_{ps} \). The esterification reaction time controlled the degree of \( \text{C}_{18}\text{H}_{37}\text{O} \)-silicon surface coverage and hence the relative amount of steric effect. The magnitude of the steric repulsion determined the amount of depletion polymer required to overcome the repulsion and effect a phase separation. Additionally, for a fixed reaction time a change in particle size distribution also changed the degree of \( \text{C}_{18}\text{H}_{37}\text{O} \) coverage. Hence the effects of particle size and esterification reaction time on the location of \( C_{ps} \) were not independent.
Figure 10: Phase separation experiment: a) 0 mg/ml. b) 0.27 mg/ml. c) 0.82 mg/ml and d) 64 mg/ml.
In a separate phase separation experiment the excess physisorbed $C_{18}H_{37}O$ was not removed from the surface of the silicon. TGA showed a total of approximately 8 wt% $C_{18}H_{37}O$ present on the powder surface. Increasing amounts of polystyrene were added to the tubes in an attempt to overcome the strong net steric repulsion resulting from the 8 wt% surface coverage. The maximum polystyrene concentration was limited only by the viscosity of the polystyrene stock solution resulting from the increasingly large amounts of polystyrene required to be dissolved in the fixed cyclohexane volume. A phase separation could not be induced at the same molecular weight of the polystyrene. After later removing the physisorbed layer of $C_{18}H_{37}O$ on the silicon surface via chloroform/cyclohexane washing, TGA showed the expected coverage of 4 wt% and subsequent phase separations were achieved at desired polystyrene concentrations.

3.2.3 Viscosity Measurements

A phase separation experiment was performed with a series of dispersions over a wide range of polystyrene concentrations (silicon mass held constant). The tubes were allowed to stand at 40°C for 8 hours to ensure a complete phase separation. The volumes of the lower phases were observed to increase with increasing polystyrene concentration as shown by the graph in figure 11. Smaller final volumes are indicative of the stability of the silicon slurry. Well dispersed
Figure 11: Lower phase volumes resulting from increasing polystyrene concentration
primary particles pack efficiently and form smaller final sediment volumes. Unstable, flocced lower phases will result in higher final volumes. The smallest final volume (2.75 ml) occurred at the polystyrene phase separation concentration $C_{ps}$ (and corresponded to 40 wt\% silicon). Thus, sediment volumes quantitatively indicate lower phase stability and aid in identifying $C_{ps}$.

After the lower phase volumes in the series of tubes at increasing concentrations were observed, the clear upper phases of all of the tubes were removed. The remaining lower phases were used for viscosity measurements. Viscosity measurements were made using a Haake Rotovisco CV100/RV100 (Haake-Buchler Instruments Inc., Saddlebrook, NJ) at a constant temperature of 25°C. Shear stress versus shear strain curves are used to identify the yield point, which indicates the stress required to break up the floccs. Higher yield stresses indicate a larger degree of flocculation and instability in the sample.

Figure 12 shows the shear stress versus shear rate curves for the series of phase separations occurring over a broad range of polystyrene concentrations. The high shear rate plateau was extrapolated to 0 s$^{-1}$ to obtain the apparent yield stress. The lower phases prepared in tubes with increasing polystyrene concentration exhibit higher yield points. The higher yield points are attributed to the increased depletion flocculation forces resulting from large amounts of the added polystyrene depletion
Figure 12: Shear rate versus shear stress curves for a series of phase separations over a broad polystyrene concentration range.
polymer. The flocculating forces are strong enough to overcome the constant steric repulsion provided by the octadecanol bonded to the silicon surface. At the phase separation concentration $C_p = 0.78\, \text{mg/ml}$, which is expected to have maximum stability, no yield stress was measured. Hence, viscosity measurements are a good predictor of lower phase stability and aid in determining the polystyrene phase separation concentration where maximum stability occurs.

3.3 Fiber Dipping

Fiber coatings of Si powder were prepared on SCS-6 SiC fibers. The SCS series of SiC fibers is produced by deposition of SiC on a continuous carbon fiber using the technique of CVD from methyl trichlorosilane onto a heated carbon monofilament which was pulled continuously through a deposition reactor. The initial fibers basically consisted of a $\sim 50\, \mu\text{m}$ layer of SiC deposited on a carbon filament of $\sim 33\, \mu\text{m}$ diameter. The more recent members of the series have an outermost carbonaceous coating that is deposited onto the SiC in the later stages of CVD by introducing hydrocarbon gas and silane vapor near the exit port of the reactor. The outermost carbonaceous layer doubles the strength of the uncoated SCS fiber. The coating consists of a carbon layer with SiC particles embedded in it. The different fibers in the series differ in the nature of the outermost coating with the inner parts being essentially the same. A detailed study of the microstructure of the SCS-6 fiber has been carried out by Ning and Pirouz (Ning, 1991). SCS-6 fibers have a
round cross-section and a filament diameter of 143 μm.

All phase separation experiments were performed with a series of tubes with increasing free polystyrene concentration (temperature and mass of silicon constant). After allowing the tubes to stand for eight hours at 40°C to ensure completeness of phase separation, the clear upper phase in all the tubes was removed. Approximately 2 cm lengths of SCS-6 fibers were dipped once into the lower phases. After allowing approximately 15-30 seconds for the coatings to dry, the fibers were mounted and prepared for examination with the electron microscope. Figures 13 through 16 compare the silicon powder coatings on the fibers at four different polystyrene concentrations in the series of increasing polystyrene concentrations. All fiber coatings are shown at two different magnifications at ×750 and ×450.

Figure 13 shows the coverage of Si powder on a fiber after dipping in a lower phase prepared with a polystyrene concentration of 64.6 mg/ml, above the flocculation concentration \( C_f \). The micrographs show a patchy, uneven coverage of powder on the fiber. In figure 14 the fiber was dipped in a lower phase slurry obtained by a phase separation at a polystyrene concentration \( C_{ps} \leq C < C_f \) (\( C = 0.82 \) mg/ml) for the system. An even, uniform silicon coverage results. In figure
Figure 13: Micrograph of silicon coated SCS-6 fiber prepared via phase separation with a polystyrene concentration above the flocculation concentration at a magnification of (a) x750 and (b) x450.
Figure 14: Micrograph of silicon coated SCS-6 fiber prepared via phase separation at a polystyrene concentration of $C_p \leq C < C_r$ ($C = 0.82$ mg/ml) at a magnification of (a) $\times750$ and (b)$\times450$. 
Figure 15: Micrograph of silicon coated SCS-6 fiber prepared via phase separation with a polystyrene concentration below the phase separation concentration at a magnification of (a) ×750 and (b) ×450.
Figure 16: Micrograph of silicon coated SCS-6 fiber prepared without polystyrene at a magnification of (a) ×750 and (b) ×450.
the polystyrene concentration (0.27 mg/ml) was significantly less than the phase separation concentration. The resulting silicon powder coverage is uneven and patchy. Finally figure 16 shows a fiber dipped in the control tube with no polystyrene present (gravity settling of Si). The fiber is bare and shows no adhesion of silicon powder to the fiber surface.

From the sequence of micrographs in figures 13 through 16 it can be seen that the quality of silicon powder coatings on the fibers is directly dependent on the stability of the lower phase resulting from the phase separation. At the phase separation concentration of polystyrene the stability of the lower phase is at a maximum as the flocculating depletion forces are balanced by the steric repulsion forces. Combined with the low viscosity and high fluidity, the resulting coatings are uniform and evenly distributed.

As the concentration of polystyrene is increased, the depletion flocculation forces begin to be stronger than the steric forces provided by the C_{18}H_{37}O barrier on the Si powder. Agglomerates begin to be formed, and the stability and fluidity of the slip decreases. When a fiber is dipped into these slips, small agglomerates are deposited on the fiber as shown in figure 13. At higher polystyrene concentrations when larger agglomerates are formed, the weight of these agglomerates may begin to be greater than the capillary and van der Waals forces of adhesion responsible for powder sticking to the fiber surface. Hence, coverage will deteriorate further until no powder adheres to the fiber.
At concentrations below the phase separation polystyrene concentration, the silicon solids are unaffected by the presence of free polystyrene. The steric stability imparted by the C_{18}H_{37}O groups on the surface of the silicon powder is insufficient to provide a thermodynamically stable slip. Hence, again agglomerates will be deposited on the fiber, and patchy, non-uniform fiber coverage results as shown in figures 15 and 16.

To determine the thickness of the silicon coating deposited on the fibers, the cross section of several fibers dipped into lower phase slips prepared near the polystyrene phase separation concentration were examined with an electron microscope. The micrograph in figure 17 shows the cross section of a SCS-6 fiber dipped twice in the lower phase prepared at a concentration C_{ps} \leq C < C_f. The carbon core surrounded by silicon carbide and a double layer of carbon is covered by a uniform, well packed thick layer of silicon deposited during the two dips. The thin bright layer surrounding the silicon layer is a layer of sputter coated gold which was used to protect the silicon layer during the fiber mounting and polishing process. The different regions are delineated in figure 18 which shows a silicon coating from one dip which resulted in a 1 - 1.5 \mu m thick coating. The micrograph in figure 19 shows
Figure 17: Micrograph of the cross section of an SCS-6 fiber showing thickness and uniformity of the silicon coating.

Figure 18: Micrograph of the cross section of an SCS-6 fiber dipped once showing thickness and uniformity of the silicon coating.
Figure 19: Micrograph of the cross section of an SCS-6 fiber dipped twice showing thickness and uniformity of the silicon coating.

Figure 20: Micrograph of the cross section of an SCS-6 fiber dipped three times showing thickness and uniformity of the silicon coating.
an SCS-6 fiber dipped twice in silicon slurry. It can be seen that two dips gave 2 - 2.5 μm thick coatings. Three dips resulted in an approximately 6 μm thick coating as shown in figure 20. Silicon powder in smaller, more monodisperse size distribution resulted in slightly thinner coatings. However due to the smaller and more spherical size of the particles the coatings were more uniform, densely packed and less porous. The cross sections shown in the micrographs in figures 17 through 20 and all other cross sections viewed with the SEM showed coatings highly uniform in thickness throughout.

The powder used in the above described experiments was attrition milled in 300 gram batches for 24 hours. The resulting powder was irregular and platelike in shape. While good silicon coatings could be achieved with this powder as described above, better coatings can be obtained using smaller, more spherical primary particles. A separate set of phase separation experiments was performed analogous to those described above, but with smaller, more spherical and less angular shaped particles. The powder used in these experiments was attrition milled in 100 gram batches for 72 hours with the same amount of milling media as was used for the 300 gram batch milling. The series of micrographs in figure 21 contrast the difference in particle shape, size and hence surface area. Two different magnifications of the powder are shown. The micrographs at a magnification of ×15,000 demonstrate the change in the
Figure 21: Micrographs of silicon powder milled for 24 hrs in a 300 gram batch at a magnification of (a) $\times15,000$ and (b) $\times2,000$. 
Figure 21: Micrographs of silicon powder milled for 72 hrs in a 100 gram batch at a magnification of (c) ×15,000 and (d) ×2,000.
shape of the primary particles from angular platelike to uniform spherical as a result of the extended milling time. The micrographs at a magnification of ×2,000 show the frequency of occurrence of larger angular platelike particles over a greater sample size in the 300 gram/24 hours batch contrasted to the large distribution of fines for the 100 gram/72 hours silicon particles.

A particle size distribution analysis was performed with a combination of a Microtrac Particle Size Analyzer (Leeds and Northrup Company, Largo, Fl.) and a Nicomp Submicron Particle Size Analyzer (model 370, Santa Barbara, Ca.) to cover a range in particle sizes. The particle size distribution analysis indicated that smaller batch sizes and longer milling times broke down the larger particles and resulted in a narrower distribution of finer particles. Table 4 shows a comparison of the particle size distribution of both powders on a volume basis. A BET analysis was also performed on both powders.

<table>
<thead>
<tr>
<th></th>
<th>range (μm)</th>
<th>mean (μm)</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300g, 24hrs</td>
<td>0.17 - 2.6</td>
<td>0.785</td>
<td>16</td>
</tr>
<tr>
<td>100g, 72hrs</td>
<td>0.136 - 0.231</td>
<td>0.174</td>
<td>64</td>
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A series of phase separation experiments were performed to identify the phase separation polystyrene concentration for the smaller size silicon particles. The phase separation concentration was determined to be approximately 2.7 mg/ml. This can be compared to the phase separation concentration of 0.82 mg/ml determined for the
larger sized silicon particles. The order of magnitude difference in the phase separation concentrations is believed to be a result of a combination of the larger surface area per gram of the primary particles, and the extended esterification reaction time of the smaller size, more spherical particles. The larger silicon particles were esterified for 2 hours, while the smaller particles had an esterification reaction time of 6 hours. Smaller particles, with a greater surface area per gram, that are covered with a denser layer of C_{18}H_{37}O molecules will provide a greater steric repulsion. The increased steric repulsion provided to the silicon particle surface has been qualitatively observed through significantly increased dispersion times and decreased sedimentation rates as detailed earlier. Increased steric repulsion has also quantitatively been measured indirectly via TGA studies as detailed earlier. As a result, an increased level of polystyrene depletion polymer is required to overcome the increased steric effect and to induce the phase separation, resulting in the significantly larger phase separation polystyrene concentrations.

The micrographs in figure 22 contrast the quality of silicon coatings obtained at the respective phase separation polystyrene concentrations for each powder system. Figure 22a shows an SEM micrograph of silicon coatings obtained from the larger sized silicon particles with a polystyrene concentration of 0.82 mg/ml at a magnification of ×13,000. All coatings obtained at this concentration were dense and
Figure 22: Micrographs comparing the quality of silicon coatings on fibers prepared at the optimum polystyrene concentration for (a) 24 hrs, 300 gram grind and (b) 72 hrs, 100 gram grind.
of a consistently good quality throughout. However these coatings can be contrasted to the superior coatings achieved with the smaller, more spherical particles at a concentration of 2.7 mg/ml as shown in the micrograph at a magnification of ×13,000 in figure 22b. Small, more spherical particles result in much more even, close packed powder coatings. The porosity and uniformity of particle distribution appears to be significantly reduced when angular, platelike particles are replaced by smaller, more spherical primary particles.

Changes in particle size and shape resulting from different milling schedules significantly affected the fluidity of the lower phase at the optimal polystyrene concentration. The interface between the clear upper phase and silicon rich lower phase was almost rigid with the larger particle size batch while the smaller sized silicon particles exhibited a very fluid interface. This is indicative of the decrease in the viscosity of the silicon slurry when the finer particles were used. The viscosity of the particulate slurry is an important parameter in the success of the infiltration process. Hence it is believed that the smaller particles exhibiting lower viscosities are a better candidate for fiber weave infiltrations. Additionally, by their geometry the larger more angular particles may potentially physically block infiltration routes for other particles through the small fiber-to-fiber voids.

The range of polystyrene concentrations covered in the phase separations experiments for the smaller sized silicon particles was very broad. From the SEM
micrographs it was observed that the window of high quality coatings in the
concentration range $C_{ps} \leq C < C_r$ before any deterioration in coating quality occurred
was approximately from 0.78 mg/ml to 3.9 mg/ml. For the larger sized silicon
powder, the location of the phase separation concentration was more critical. The
decrease in coating quality was apparent within approximately 0.5 mg/ml of $C_{ps}$,
resulting in a smaller optimum concentration span $C_{ps} \leq C < C_r$. The increased steric
effect from the denser $C_{18}H_{37}O$ layer combined with the smaller, more uniform
particle size appears to result in a greater flexibility in polystyrene concentration used
in the technique to obtain high quality coatings.

The series of micrographs in figure 23 illustrate the complete range of SEM
micrographs of the SCS-6 fiber coatings for phase separations involving the smaller
sized silicon particles. All micrographs are at a magnification of $\times 5,000$. The fiber
coating in figure 23a was prepared in the reference slurry prepared with no
polystyrene present. Figure 23b shows the fiber coating at 2.7 mg/ml, the phase
separation polystyrene concentration. The coatings in both figures 23a and 23b are of
a high quality, showing a uniform silicon particle distribution with little porosity.
Although it may be difficult to distinguish from the micrographs presented here, it
was qualitatively observed that figure 23a and all other fibers dipped in the reference
slurry showed some degree of agglomerate deposition on the surface. All fibers
Figure 23: Micrographs of silicon coatings on fibers prepared at (a) zero polystyrene concentration and (b) the phase separation concentration of 2.7 mg/ml for silicon powder milled for 72 hrs in 100 gram batches.
Figure 23: Micrographs of silicon coatings on fibers prepared (c) above the flocculation concentration and (d) at extremely high polystyrene concentration for silicon powder milled for 72 hrs in 100 gram batches.
Figure 23e: Micrograph at a magnification of \times 13,000 showing glazed fiber surface coating at extremely high polystyrene concentration.
dipped in the slurries prepared in the concentration region $C_{pA} \leq C < C_f$ such as in figure 23b showed only primary particles and no deposition of agglomerates on the fiber surface.

The coatings obtained at a zero polystyrene concentration for the smaller sized silicon particle experiments contrast to the coating shown in figure 16. also prepared at a zero polystyrene concentration. The fiber in figure 16 was part of a series of fibers dipped in lower phases consisting of the larger sized particles. No coating was obtained in this case. It is believed that the absence of a coating was due to the larger size of the primary particles and the reduced steric effect of these particles resulting from a shorter esterification reaction time. As a result, the degree and rate of agglomeration in the absence of any depletion polymer was much greater. Hence the particle preference was to flocc to each other, and the weight of these floccs prevented any particle agglomerate adhesion to the surface of the fiber during the vertical dipping process.

Figure 23c illustrates the deterioration of the fiber coatings which occurs at polystyrene concentration above the flocculation concentration. The fiber coating in figure 23c prepared at 78 mg/ml shows several small bare regions on the fiber surface. The particle distribution is not uniform and is highly porous. The deteriorating nature of these coatings was similar to the deterioration of the coatings observed in the earlier series prepared with a larger primary particle size as illustrated in figure 14.
earlier.

Figure 23d depicts a SCS-6 fiber coating prepared at a polystyrene concentration of 161.7 mg/ml, two orders of magnitude greater than the minimum flocculation concentration. When the concentration of free polystyrene is higher than the flocculation concentration, as the phase separation occurs the depletion flocculating force is greater than the steric repulsion provided by the C_{18}H_{37}O barrier. As the particles flocc together and form clusters, some polystyrene may become trapped in the clusters as they sediment down to form the lower phase. Hence the flocced lower phase also contains some polystyrene. The amount of polystyrene in the lower phase is expected to increase with higher initial polystyrene concentrations farther from the flocculation concentration. This effect is believed to be the cause of the apparently glazed coatings observed in figure 23d, which shows the fiber dipped in the silicon slurry prepared at an extreme high polystyrene concentration. It can be seen that this coating is different from all other coatings of discrete primary silicon particles on the SCS-6 fiber surface. This effect was more obvious at a greater magnification as shown in figure 23e at a magnification of \times 13,000. Figure 23d is one fiber in a series of fibers dipped into the higher range of polystyrene concentration. Similar glazed coatings were seen throughout this range. At lower concentration ranges, the glazed surface was absent and the coating quality was similar to those shown in earlier micrographs.
To determine the effect of dust or trace fiber surface impurities on the silicon coating quality, several fibers underwent pretreatment procedures prior to fiber dipping. Surface cleaning was accomplished by washing the fibers in acetone, or soaking the fibers in acetone for 5 minutes with periodic agitation. After dipping in the silicon slurry, the quality of the silicon coating on surface cleaned fibers were compared using the SEM to silicon coatings on fibers that did not undergo any pretreatment procedure. The surface cleaning procedure did not appear to have any effect on the silicon coating quality or uniformity. SCS-0 fibers were also dipped in the silicon slurries both with and without surface cleaning. Again, these coating appeared to be unaffected by surface cleaning pretreatment procedures. The quality of SCS-0 coatings appeared to be identical to SCS-6 coatings.

3.4 Fiber Weave Infiltrations

3.4.1 Procedure

The phase separation experiments and SCS-6 fiber coatings described above were used to determine optimum conditions of lower phase slip stability. A phase separation based on these optimum parameters was scaled up for weave infiltration experiments. 1-10 μm silicon powder (Union Carbide, lot #50054) was attrition milled in cyclohexane for 72 hours. A particle size analysis obtained using a Nicomp
Submicron Particle Sizer (model 370, Santa Barbara, Ca) showed the silicon was milled to 0.136-0.23 μm. A thin steric barrier of approximately 3.7 wt% was provided to the silicon particles by chemically reacting 1-octadecanol (Aldrich Chemical Company) to the surface silanol groups. Concentrated dispersions of the resulting silicon-C$_{18}$H$_{37}$O powder were obtained via phase separations resulting from the depletion stabilization/flocculation phenomena. Monodisperse polystyrene (Pressure Chemical Company) with molecular weight 5780 was used as the depletion stabilization additive. The pseudo esterification reaction and phase separation experiments proceeded exactly as described in detail earlier.

5 wt% silicon-C$_{18}$H$_{37}$O was ultrasonically dispersed (model W-225 Ultrasonic Processor, Heat Systems, Inc., Farmingdale, NY) in cyclohexane in a separatory funnel. A stock solution of polystyrene was pipetted to the silicon dispersion. The total polystyrene concentration was 0.78 mg/ml. The dispersion was thoroughly mixed and tightly stoppered to prevent evaporation of the cyclohexane. The separatory funnel was allowed to stand in a water bath at 40°C. Within an hour two phases separated by a sharp interface could be distinguished. A clear upper phase was believed to be rich in polystyrene while the dark lower phase was rich in silicon. Up to 24 hours was allowed to ensure completeness of the phase separation. The silicon rich lower phase was removed into a 25 ml measuring cylinder and used for fiber weave infiltrations.
A variety of fiber types and weave designs were used for infiltration experiments to determine the robustness of the technique. Initially ceramic grade Nicalon ceramic fibers (1800 denier tow. Dow Corning) in plain square weave and 8 harness satin weave styles were used for infiltration experiments. The as-received fibers are coated with M sizing (polyvinylacetate). Prior to infiltration the M sizing was burnt off at 550°C. 0.5 × 5 inch pieces of woven cloth were dipped with tweezers two to ten times into the lower phase slurries prepared as described above. The number of dips required depended on the density of the fiber weave style. Between dips the plain weave cloths required approximately 30 seconds for the cyclohexane to evaporate at room temperature depending on the weave design type. Satin weaves required several minutes to dry due to different density of the weave style. Experimental HPZ fibers (Dow Corning) woven into 8 harness satin cloth. Thornel Carbon fibers (Amoco) in a twill weave style, and Stackpole panex carbon WCG fibers (Stackpole Carbon Co.) in a plain square weave were also infiltrated.

After infiltrations with the lower phase slurries, for handleability the woven cloth pieces were dipped in a binder/plasticizer mix. The mix consisted of 16.7 wt% silicon powder ultrasonically dispersed in a mixture of 76.5 wt% tetrahydrofuran, 4.2 wt% polybutylmethacrylate (Aldrich Chemical Company) and 2.6 wt% dibutyl phthalate (Aldrich Chemical Company). The silicon was 1-10 μm Union Carbide powder attrition milled in naphtha (Cuyahoga Chemical Corporation) for 24 hours to
0.17 - 2.6 μm. Polybutylmethacrylate was added as a binder and dibutyl phthalate acted as a plasticizer.

The infiltrated Nicalon cloths were made into 1 ply and 4 ply composites. The 0.5 x 5 inch woven cloth pieces were wrapped between two 0.5 x 5 inch strips of 0.02 inch thick silicon/teflon tape. The silicon/teflon (Dupont Co., Wilmington, DE.) tape was a 90g/10g mix blended in 8 oz of naphtha, filtered to form a paste and rolled into tapes. The infiltrated cloth placed between two strips of silicon/teflon tape was cold pressed (Carver Laboratory Press, Menomonee Falls, Wisconsin) at 1000 lb. A 0.005 inch thick layer of Si₃N₄/teflon tape was placed on top and underneath the composite, which was then wrapped in grafoil graphite tape (Union Carbide, Cleveland, Oh). The Si₃N₄/teflon tape was used to aid in grafoil removal after hot pressing. The grafoil tape was used to protect the graphite die and composite. The composite was then hot pressed (Pathways Thermal Tech, City of Industry, Ca) in a vacuum to produce handleable green compacts.

Hot pressing consisted of a multistep procedure. Under a vacuum of 10⁻⁷ Torr the temperature was ramped at 10°C/min from 20°C to 175°C. The temperature was then raised at a slower rate of 2°C/min to 500°C during the binder burn off stage while 127 lb/in² pressure was applied to the sample. After binder burn off the temperature was raised from 500°C to 800°C at 10°C/min. and then held at 800°C for
15 minutes. The pressure applied to the sample was released. Nitrogen was used to aid in cooling the hot press and sample. The grafoil was removed from the composite before nitridation. For the 4 ply composites, four strips of infiltrated cloth were stacked up with a pieces of silicon/teflon tape on the top and bottom of the stack. The 4 ply composites were consolidated in the same procedure as the 1 ply composites described above.

The consolidated green composites were transferred to a horizontal nitridation furnace consisting of a recrystallized Al₂O₃ reaction tube with stainless steel end caps. The heat was provided by external silicon carbide heating elements. The composites were located in the central hot zone of the furnace where the temperature variation could be held to ±2°C. Nitriding gas of commercial purity was further purified prior to introduction into the furnace by passing through an oxygen trap. The O₂ and H₂O contents were reduced to less than 1 ppm. The composites were nitrided at 1250°C for 4 hrs with a Nitrogen flow of 3 ft³/hr at atmospheric pressure.

3.4.2 Experimental Results and Discussion

A variety of weaves of different design and fiber types were infiltrated, consolidated and nitrided by the above described procedure. Figures 24 through 29 show a series of SEM micrographs of the different weaves. Each figure shows two
different magnifications of the same cross section of infiltrated composite. The micrographs presented here were chosen as representative of the overall quality of infiltration seen throughout the composite. Initial infiltration experiments were performed with Nicalon silicon carbide fibers. Nicalon ceramic fiber is a multifilament silicon carbide fiber manufactured through a polymer pyrolysis process by Nippon Carbon Co., Ltd., of Japan and is available in North America from Dow Corning Corporation, Midland, Michigan. The fiber is homogeneously comprised of ultrafine beta-SiC crystals with excess carbon and 9 to 11 percent oxygen as SiO₂ (58 % silicon, 31 % carbon, 11 % oxygen). The fiber has excellent strength properties, retains its properties at high temperatures, and is highly resistant to oxidation and chemical attack. Nicalon fiber is available in three different grades (differentiated by their electrical properties), several physical forms (continuous fiber supplied as a multifilament tow, chopped fiber and woven cloth available in three standard weave styles: plain, 8 harness satin, 12 harness satin), surface treatments, sizing options (polyvinylacetate “M”-sizing, polyvinylalcohol “PVA”-sizing or a modified epoxy “P”-sizing) and denier options. There is some variety in the cross-sectional size and shape of the fibers (round to oval). There are 250-500 filaments/tow and the fiber diameter is approximately 12-15 μm.

Cross-sectional areas of infiltrated and nitrided 1-ply and 4-ply composites were examined with the Scanning Electron Microscope. Figure 24 shows two
Figure 24: Micrograph of infiltrated 1 ply Nicalon square weave composite at a magnification of (a) \( \times 500 \) and (b) \( \times 200 \).
Figure 25: Micrograph of infiltrated 1 ply Nicalon satin weave composite at a magnification of (a) ×500 and (b) ×250.
Figure 26: Micrograph of infiltrated 4 ply Nicalon satin weave composite.
Figure 27: Micrograph of infiltrated 1 ply Stackpole Panex C fiber square weave composite at a magnification of (a) ×500 and (b) ×250.
Figure 28: Micrograph of infiltrated 1 ply HPZ satin weave composite at a magnification of (a) ×500 and (b) ×200.
Figure 29: Micrograph of infiltrated 1 ply C Thornel fiber satin weave composite at a magnification of (a) $\times500$ and (b) $\times250$. 
different magnifications of the same cross-section of a 1-ply Nicalon plain square weave. The infiltration of matrix powder is good across the cross-section. Figure 25 shows the cross section of an infiltrated 1 ply satin weave composite. The square weave was measured to be approximately 0.013 inch thick while the satin weave was 0.027-0.035 inches thick. A 4 ply satin composite is also shown in figure 26. Both weave design styles of Nicalon fibers were uniformly infiltrated throughout.

Stackpole Panex carbon WCG fiber is a non continuous pitch based fiber. Small lengths of fibers are spun into thread which is woven into different weave styles. As a result, the shape of the fiber is circular with a highly jagged, irregular surface. Figure 27 shows micrographs of an infiltrated square weave of these carbon fibers. The weave was very lightweight and fine with a thickness of 0.005 to 0.007 inches. Thus it was difficult to infiltrate via the dipping procedure without creasing and crumpling the weave as it was lowered into the slurry. As a result, this weave was only dipped three times in the depletion stabilized silicon slurry. From the micrographs however, it can be seen that despite these difficulties and surface irregularities a very high quality and uniform infiltration was achieved.

X9-6371 HPZ ceramic fiber (Dow Corning Corporation, Midland, Michigan) is an inorganic silicon nitride type fiber manufactured by a polymer pyrolysis process prepared from hydridopolysilazane polymer. The ceramic fiber is amorphous with a typical elemental composition of 57 % silicon, 28 % nitrogen, 10 % carbon and 4 %
oxygen. The fiber has excellent tensile strength and modulus as well as high volume resistivity. At this time HPZ fibers are a developmental/experimental product which is constantly undergoing improvement and is not commercially available (limited sampling only). There are 200-800 filaments/tow. The filament diameter is 10 - 12 \( \mu \text{m} \). The weave thickness was approximately 0.011-0.012 in thick. The product is supplied with surface treatments and sizing. HPZ fiber is available as continuous yarn which can be woven into various weave styles.

The micrographs in figure 28 show the cross section of a 1 ply satin weave of HPZ fibers. The weave was dipped five times in the depletion stabilized silicon slurry. The elongated oval fiber geometry contrasts to the highly spherical Nicalon fibers. The distribution of HPZ fibers in the weave does not appear as ordered as in the Nicalon weaves and varies greatly in density throughout the weave. The micrographs show the infiltrated HPZ satin weave is highly loaded with matrix powder throughout.

Thornel carbon fiber T-650/35 (Amoco Performance Products, Ridgefield, CT) is a continuous length, high strength, high modulus fiber made from a polyacrylonitrile precursor. The fiber surface had been treated to increase the interlaminar shear strength in a resin matrix composite. The fiber surface consists of oxidized carbon functionality with minor levels of silicon, oxygen, nitrogen and sulfur contaminants. There are 3000 filaments/strand and the filament diameter is 6.8\( \mu \text{m} \).
The thickness of the weave was 0.014-0.016 inches.

The cross-sectional fiber shape is mostly round with some “kidney-bean” shape. In contrast to the smooth surfaces of the SCS-6 and Nicalon fibers, the surface of Thornel carbon fibers consists of cranulated groves resulting from the process of spinning the polyacryonitrile precursor. The density of the filaments/tow is approximately 4 to 15 times the density of the fibers in the HPZ satin weave and 6 to 12 times the density of the Nicalon weaves. Despite such a high filament density, the fiber surface roughness, the fiber kidney-bean shape and the irregular fiber orientation, the micrographs in figure 29 show good infiltration of matrix powder throughout. The cross section is again highly loaded with powder and has very low voidage throughout.

The series of micrographs in figures 24 through 29 show high quality infiltrations throughout. All the weave styles and fiber types attempted in infiltration experiments are highly loaded with matrix powder and show low voidage. The quality of these infiltrations can be compared to infiltrations in silicon powder slurries prepared via other techniques. Nicalon square weaves have been dipped into slurries of silicon powder in cyclohexane solvent (Babuder, 1993). The bare, untreated silicon powder with an oxidized silanol and siloxane surface was milled for 72 hours. No esterification or other surface treatment was performed. The silicon powder was ultrasonically pulsed in the cyclohexane solvent to break up any agglomerates that
may be present prior to dipping the cloth strips into the slurry.

Composites infiltrated via this powder preparation technique were examined with the scanning electron microscope. The cross section of the Nicalon square composites showed minimal infiltration with matrix powder. Infiltration occurred primarily as a surface layer, with little to no infiltration towards the center of the cloth. The voidage was high throughout. We believe that the poor infiltration quality obtained via this technique results from the rapid flocculation of the untreated silicon powder. In the absence of any repulsive stabilization mechanism (steric layer), and in the poor cyclohexane dispersive medium for silicon, after ultrasonication the onset of flocculation of the primary silicon particles is rapid. The larger, irregular shape and size of the agglomerates cannot physically infiltrate the small fiber-to-fiber spaces. As a result the agglomerates tend to deposit on the outer surface of the cloth, thereby providing a physical barrier and blocking any further possible weave infiltration routes during later immersion in the slurry. Despite the simplicity and ease of such slurry preparation, this technique results in poor infiltrations.

Infiltrations have also been performed using a silicon-acetone slurry (Babuder, 1993). 25 wt % of silicon was ultrasonically dispersed in acetone to break up any agglomerates. The silicon was 1-10 μm Union Carbide powder attrition milled in naphtha for 24 hours to 0.17-2.6 μm size. The silicon was not treated and no additives were used in the acetone slurry. Infiltrations followed the same dipping.
composite consolidation and nitridation procedure as outlined for the depletion stabilization slurries above. To ensure that no agglomerates formed between weave dips, the silicon/acetone slurry was ultrasonically pulsed at intervals. Composites prepared via acetone slurries were also examined under the scanning electron microscope. The infiltration quality of these slurries was a significant improvement over the cyclohexane slurries. There was, however, a noticeable level of voidage. Acetone is a good solvent for silicon dispersion (Bleier, 1983). Although the silicon particles remained well dispersed after ultrasonic pulsing, a small degree of flocculation could qualitatively still be observed to be occurring. Hence continued ultrasonic treatment at intervals was necessary. Due to the unavoidable generation of some flocculation, infiltration was improved but not complete. Additionally, as a result of the heat generated by the continued ultrasonic pulsing to prevent agglomerate formation, rapid evaporation of the acetone solvent was a problem.
Analyzes were performed on the fiber coating obtained via dipping and the fiber bundle penetration by the slurry. These simplified models were intended to identify the governing parameters and establish trends which dominate these processes. The guidelines determined by these analyses can be used for the automation or scale up of the fiber weave penetration operation.

4.1 Fiber Coating Thickness

Analytical models for the fiber coating operation and the penetration of the slurry into the fiber tows were developed to determine the important parameters affecting these processes. The results from the analyses are compared to the experimentally determined fiber coating thickness and the observations of the fiber tow penetration and drying. The models include the non-Newtonian behavior of the slurry which was characterized by the viscosity measurements described previously in section 3.2.3.

The application of liquid coatings to solid surfaces is frequently encountered in commercial processes. An analysis of the problem of predicting the film thickness as a function of withdrawal speed and the physical properties of the fluid has been previously studied for a flat plate geometry for both Newtonian (Spiers, 1974) and
non-Newtonian fluids (Spiers, 1975). However the analysis performed herein considers the coating of a non-Newtonian fluid onto a vertical fiber surface continuously withdrawn from the fluid bath. The fiber coating thickness, $\delta$, is determined to be a function of the fiber pulling speed, $U$, and fluid density, $\rho$, and the parameters of the viscous model used. The analytic treatment presented here also predicts the velocity profile of the fluid on the fiber surface in the region of constant coating thickness as a function of fiber pulling speed.

Figure 30 shows the profile of a liquid film adhering to a vertical moving surface. The vertical surface is a cylindrical fiber continuously withdrawn from a large bath of non-Newtonian fluid. For the analysis presented here, the liquid bath represents a stabilized dispersion of silicon particles in cyclohexane solvent. Four forces are normally considered: viscous, gravity, surface tension and inertia. If the problem is limited to relatively slow speeds (creeping flow), the inertial forces can be neglected. An analysis of the fiber coating conditions in the fiber dipping experiments described previously showed that the creeping flow assumption is valid with an approximate Reynolds number of less than 2 for fiber speeds less than 100 cms$^{-1}$. The liquid film can be considered in five regions as illustrated in figure 30. In region 1 close to the surface of the bath, flow effects can be neglected to a first approximation and only surface tension forces are considered. Region 2 is referred to as the dynamic meniscus region in which the film thickness varies with the height
Figure 30: Profile of a liquid film adhering to vertically moving fiber.
above the bath. The viscous, gravity and surface tension forces all have to be taken into account. Region 3 is the region far from the surface of the silicon/cyclohexane dispersion bath where the film thickness becomes constant at \( \delta_f \). Only viscous and gravity forces are significant in this region. Above region 3 the film begins to dry. Region 4 represents a transitional region in which the solvent in the slurry evaporates. After evaporation is complete a dry layer of solid particles of thickness \( \delta_f \) remains, as shown in region 5.

For this analysis we consider the film in region 3, the constant film thickness region. The coordinate system is defined as depicted in the schematic diagram in figure 30. The equation of motion for the non-Newtonian fluid of density \( \rho \) is:

\[
0 = -\frac{1}{r} \frac{\partial}{\partial r} (r \tau_r) - \rho g
\]  

(7)

By using the boundary condition:

\[
\tau_r(a + \delta_f, z) = 0
\]

where \( a \) is the fiber radius, equation 7 can be integrated to yield:

\[
\tau_r = -\frac{\rho g}{2} r + \frac{\rho g}{2} (a + \delta_f)^2 \left( \frac{1}{r} \right)
\]  

(8)

Several empirical equations have been proposed to express the steady state relation between \( \tau_r \) and \( \partial \tau_r / \partial r \) for non-Newtonian fluids. Each of these models contain empirical positive parameters which can be evaluated numerically to fit data on \( \tau_r \) versus \( \partial \tau_r / \partial r \) at constant temperature and pressure. The two parameter
equation called the Ostwald-de Waele model (Bird, 1960) is also known as the power law:

$$\tau_\eta = -m \left| \frac{\partial v_z}{\partial r} \right|^n \frac{\partial v_z}{\partial r} \tag{9}$$

For $n = 1$ it reduces to Newton’s law of viscosity with $m = \mu$. Thus the deviation of $n$ from unity indicates the degree of deviation from Newtonian behavior. For values of $n$ less than unity, the behavior is pseudoplastic. For $n$ greater than unity the behavior is dilatant.

The form of the power law given in equation 9 was used in this analysis to describe the pseudoplastic behavior of the silicon lower phase slurries formed via the depletion stabilization technique. These slurries were used to deposit a coating of silicon powder on the surface of cylindrical SCS-6 fibers as modeled here. Using the shear rate verses shear stress data obtained for the critical limiting concentration of 0.79 mg/ml. the power law parameters for the best fit of data were $n = 0.5$ and $m = 0.2$ kg·m⁻¹·sⁿ. Figure 31 shows the shear rate versus shear stress data for the optimum slurry stability conditions and the best fit. To use the power law model, one must first eliminate the absolute value sign. Because the velocity gradient is everywhere negative for this problem, the power law becomes:

$$\tau_\eta = -m \left| \frac{\partial v_z}{\partial r} \right|^n \frac{\partial v_z}{\partial r} = m \left( -\frac{\partial v_z}{\partial r} \right)^n \left( \frac{\partial v_z}{\partial r} \right) = m \left( -\frac{\partial v_z}{\partial r} \right)^n \tag{10}$$
Figure 31: Viscosity data fit
Equating the power law with equation 8, we obtain the relationship:

$$\frac{\partial \nu_z}{\partial r} = -\left[ \frac{\rho g}{2m} + \frac{\rho g (a + \delta_i)^2}{2m} \left( \frac{1}{r} \right)^n \right]^{1/n}$$  

(11)

When $n=1/2$, the best fit parameter from the 0.79 mg/ml critical concentration case, equation 11 above can be integrated with the boundary condition:

$$\nu_z(r = a, z) = U$$

to obtain the velocity profile:

$$\nu_z = U + \left( \frac{\rho g}{m} \right) \left[ \frac{a^3 - r^3}{12} - \frac{(a + \delta_i)^2(a - r)}{2} + \frac{(a + \delta_i)^4}{4r} - \frac{(a + \delta_i)^4}{4a} \right]$$  

(12)

The volume flux of liquid, $Q_l$, in the constant film thickness region is given by:

$$Q_l = \int_0^{\pi} 2\pi r \nu_z dr$$  

(13)

which when integrated yields:

$$Q_l = U \pi [(a + \delta_i)^2 - a^2] + \left( \frac{\rho g}{m} \right)^2 \pi \left[ \frac{(a + \delta_i)^2 a^3 - a^5}{12} + \frac{a^5 - (a + \delta_i)^5}{30} \right.$$  

$$+ \frac{(a + \delta_i)^3 a^3 - 2(a + \delta_i)^4 a + (a + \delta_i)^5}{2} +$$  

$$\frac{(a + \delta_i)^3 - (a + \delta_i)^4 a^2}{3} + \frac{(a + \delta_i)^4 a^2 - (a + \delta_i)^6}{4a} \right]$$  

(14)

The volume flux of material on the withdrawing fiber is dependent on the liquid film thickness $\delta_i$, where $\delta_i$ is determined by the complicated interaction of the surface tension and viscosity of the fluid in region 2.
In the transitional area (region 4) the solvent evaporates, leaving the suspended particles in the slurry as a solid coating on the fiber (region 5). The dry solid coating moves as a plug flow with fiber speed $U$ and a total volume flux given by:

$$ Q_s = U \pi [(a + \delta_s)^2 - a^2] $$  \hspace{1cm} (15)

The total volume flux of solid in the liquid layer can be equated with the volume flux in the solid film:

$$ Q_s \varphi_s - Q_l \varphi_l = 0 $$  \hspace{1cm} (16)

where $\varphi_s$ and $\varphi_l$ are the fraction volume of solids in the solid and liquid films, respectively. For the fiber dipping experiments described earlier, the weight percent of solids was 40 wt%, which corresponds to a volume fraction of $\varphi_l = 0.2$. The volume fraction of solids in the dried film is estimated to be $\varphi_s = 0.8$.

Equation 16 contains two unknowns, $\delta_s$ and $\delta_l$ for a given fiber pulling speed. Choosing a value for $\delta_l$, and hence the solid flux on the fiber, fixes $\delta_l$. A range of solid film thicknesses yields a corresponding set of liquid film thickness solutions satisfying the relationship in equation 16. Ideally one could estimate $\delta_l$ from the fluid properties and pulling speed in region 2. Many authors have proposed correlations for the flux of material on the fiber versus liquid film thickness (Groenveld 1970, Gutfinger and Tallmadge 1965). In most instances only the maximum film thickness is predicted due to the complicated nature of region 2. In this analysis we also will only set an upper limit for the liquid film thickness without concern for the effects in
region 2. Figure 32 shows the function in equation 16 plotted against the liquid film thickness for a single pulling speed \( U = 0.01 \text{ cm/s} \). Each curve represents a different solid film thickness. Equation 16 depends on \( \delta_x^2 \) and exhibits a parabolic shape as shown in the curves. When there is sufficient liquid flux on the fiber to equal the solidified film flux there are at most two roots to the equation, as shown in the figure. Consider the case for a withdrawal speed \( U = 0.01 \text{ cm/s} \). For a solid film thickness \( \leq 5.5 \text{ \mu m} \), the corresponding liquid film thickness is determined by the first zero crossing of the function in equation 16. However, as the solid film thickness increases > 5.5 \text{ \mu m} the curves no longer cross zero. There is insufficient liquid flux on the fiber to match the solid flux set by \( \delta_x > 5.5 \text{ \mu m} \). The case where \( \delta_x = 5.5 \text{ \mu m} \) corresponds to the maximum liquid film thickness, where \( \delta_r = 24 \text{ \mu m} \) for the \( U = 0.01 \text{ cm/s} \) fiber pulling speed. The graphical procedure above was used to determine the maximum liquid film thickness for each pulling speed \( U \). The value of \( \delta_x \) required to yield a curve which was tangent to the \( y=0 \) line determined the maximum \( \delta_x \). The shapes of the curves for the faster pulling speed cases were of similar form to that shown in figure 32.

The zero crossing points to the left of the \( (\delta_x = 5.5 \text{ \mu m}) \) tangency point were selected as the correct roots and can be explained as follows. There are two liquid film thicknesses which satisfy the flux requirements in equation 16 for solid film
Figure 32: Graphical procedure for determining the maximum liquid film thickness.
thicknesses < 5.5 µm. Intuition tells us that the root representing the smaller film thickness must be more probable than the larger film thickness since the smaller film thickness is closer to the final solidified film thickness. The velocity profiles for these two liquid film thicknesses have very different characteristics. The small film thickness will have a relatively flat velocity profile. However, the large film thickness solution will exhibit a large amount of shear across the film, and therefore have a significantly lower outside film velocity. In the extreme, the large film thickness velocity profiles may exhibit enough shear that the velocity profile becomes negative at the outer regions of the film. An example of this high shear velocity profile and the relatively flat velocity profile for the small film thickness are depicted in figure 32. For comparison with these two profiles, the velocity profile for the 0.01 cm/s case is shown in figure 33. The velocity profiles shown in both insets in figure 32 are normalized by the fiber pulling speed U. The velocity profile in the left inset is plotted for the first zero cross of the δₐ = 1.5 µm curve, which occurs at a liquid film thickness of 6 µm. The velocity profile shown in the right inset is for the second zero cross on the δₐ = 1.5 µm curve and has a corresponding liquid film thickness of 36 µm. A velocity profile exhibiting a negative velocity region is physically impossible for the fiber coating operation being modeled. There can be no fluid falling off of the fiber in region 3 under the steady state conditions assumed to exist in this region. Hence, the roots to equation 16 which lie to the left of the tangent line case are the only physically realistic solutions. Therefore, the maximum film thickness occurs
Figure 33: Normalized velocity profiles for liquid coated fibers.
when the two zero crosses become a single root at the point of tangency to the $y=0$ line. No more physically possible roots exist to the right of this point.

Using the maximum liquid film thicknesses determined above and equation 12, the velocity profiles normalized by the fiber pulling speed for five speeds ($U=100, 10, 1, 0.1, 0.01$ cm$s^{-1}$) for a $100 \mu$m diameter SCS-6 fiber were computed and are shown in figure 33. The liquid film thickness is indicated by the radial extent of the velocity profile. As the pulling speed increases, the liquid film thickness on the fiber increases. The viscous forces overcome the gravity forces, yielding larger film thicknesses. The shapes of the velocity profiles show a trend of slower change in relative velocity with increasing radius. The trend is indicative of the increasing shear region which entrains more fluid onto the fiber. The solid film thicknesses are also listed in the figure, and follow the same trend as the liquid film thicknesses.

The fastest pulling speed corresponds to a $Re = 2$ based on the $\Delta v$ between the fiber surface and the fluid, and the film thickness. Hence, the previous creeping flow assumption is valid up to this pulling speed. The other interesting feature in figure 33 is the shape of the velocity profiles, which maintain the no shear boundary condition at the liquid/air interface, hence the horizontal section of the profiles at the edge of the liquid film.

The estimated pulling speed for the experimental fiber dipping was
approximately 0.3 cms⁻¹. The actual fiber coatings were measured to be
approximately 2 μm, which is smaller than the maximum predicted value of roughly
15 μm for this pulling speed. The shape of the meniscus in region 2 determines the
actual liquid film thickness as the fiber is withdrawn from the bath. More detailed
information on the meniscus in region 2 is required to determine the actual liquid film
thickness. The transitional region 4 also significantly influences the final solid film
thickness. The observed film thickness indicates that we are not operating under the
conditions of the maximum possible liquid film thickness. The minimum thickness
which could be obtained from the fiber dipping process is zero, since it is possible to
have no liquid film adhering to the fiber under the conditions of low velocity where
the film runs off the fiber before solidifying.

The evaporation time for a thin film of cyclohexane solvent on a cylindrical
fiber was estimated. The air surrounding the fiber was assumed to be quiescent, with
a minimal amount of convection. The mass transfer coefficient for the cyclohexane
evaporation was obtained from the Nusselt correlation (Robinson. 1987) and (Welty.
1976) for very thin wires:

\[
\frac{k_e \delta}{\delta} = a[N_{en} \, N_{en}]^{\pi} = a \left[ \left( \frac{\delta \, \rho \, g \, \Delta \rho \, \sigma}{\mu^2} \right) \left( \frac{\nu}{\delta} \right) \right]^{\pi}
\] (17)

where \( k_e \) is the mass transfer coefficient, \( \delta \) is a characteristic length. \( \delta \) is the
diffusivity of cyclohexane vapor in air, \( g \) is the gravitational constant. \( \mu \) is the
viscosity of cyclohexane. $\rho$ is the density of the cyclohexane, and $\Delta \rho_x$ is the density difference between the cyclohexane vapor just outside the film and the surrounding air, which drives the buoyancy flow. The constants $a$ and $m$ depend on the geometry. and for thin wires are 1 and 0.1, respectively. Solving equation 17 for $k_\tau$ gives:

$$k_\tau = \frac{8}{\delta} \left[ \left( \frac{\delta^3 \rho g \Delta \rho_x \nu}{\mu^2} \right) \left( \frac{\nu}{\delta} \right) \right]^{0.1}$$

(18)

Setting the quantity in brackets raised to the 0.1 power equal to $\Gamma$ we get a simple expression for the mass transfer coefficient:

$$k_\tau = \frac{8 \Gamma}{\delta}$$

(19)

The quantity $\Gamma$ contains the product of the Grashoff and Prandtl numbers raised to a small power, and thus is on the order of magnitude of 1 even for a large range of values. For characteristic length $\delta$ equal to the fiber radius plus a liquid film thickness of 24 $\mu$m, cyclohexane viscosity $\mu=2$ g cm$^{-1}$ s$^{-1}$, cyclohexane density of 1.36 g cm$^{-3}$, cyclohexane vapor-air density difference of $2.3 \times 10^{-3}$ g cm$^{-3}$, and $\delta$ equal to $7 \times 10^{-2}$ cm$^2$s$^{-1}$, the value of $\Gamma$ is 0.2. The diffusivity was calculated using the kinetic theory of gases coupled with the Lennard-Jones intermolecular potential (King, 1980).

A mass balance on the film covering the cylindrical fiber gives an expression for the loss of material from the evaporating film:
\[ -\frac{\partial m_{\text{film}}}{\partial t} = 2\pi r L k_i C_{sa} \]  \hspace{1cm} (20)

where \( m_{\text{film}} \) is the mass of the fluid coating on the cylinder, \( k_i \) is the mass transfer coefficient of cyclohexane in air, \( C_{sa} \) is the saturated vapor concentration and \( L \) is the length of the fiber. Rewriting in terms of volume \( V \) of the film and density \( \rho \) of the cyclohexane yields the expression:

\[ -\rho \frac{\partial V}{\partial t} \frac{\partial r}{\partial t} = 2\pi r L k_i C_{sa} \]  \hspace{1cm} (21)

which when substituting in the surface area of the cylinder yields:

\[ -\rho 2\pi r L \frac{\partial r}{\partial t} = 2\pi r L k_i C_{sa} \]  \hspace{1cm} (22)

The mass transfer coefficient can be approximated as \( k_i = \frac{\Delta}{r} \) using the result from equation 19 and then substituted into equation 22. After integrating with the initial condition \( r = a + \delta t \) at \( t = 0 \) gives:

\[ (\delta_i + a)^2 - r^2 = \frac{2\delta \Gamma C_{sa}}{\rho} t \]  \hspace{1cm} (23)

which when rearranged for \( r = a \) (where the liquid film has completely evaporated down to the fiber surface) gives:

\[ t = \frac{[(\delta_i + a)^2 - a^2] \rho}{2\delta \Gamma C_{sa}} \]  \hspace{1cm} (24)

Hence, the evaporation time is dependent on the film thickness, fiber radius, diffusivity, slurry density, saturated vapor concentration and the product of the Grashof and Prandtl numbers contained in \( \Gamma \). The saturated concentration of
cyclohexane vapor surrounding the fiber is essentially just the density of pure cyclohexane vapor \( C_{sat} = 0.0035 \, \text{g/cm}^3 \). For the range of film thicknesses found in the analysis, the characteristic drying times are approximately 10 s for the 290 \( \mu \text{m} \) film and 0.4 s for the 24 \( \mu \text{m} \) film. This simple analysis neglects the presence of the silicon particles in the fluid and any heat transfer to the film. After the initial surface cyclohexane evaporation, as the solid film begins to form on the fiber surface, the remaining cyclohexane must diffuse through the porous silicon layer. These calculated evaporation times represent the fastest drying times. The presence of the silicon particles extends the drying time. Drying times longer than those presented here, which account for the presence of the Si particles would agree with the observed drying times on the order of seconds.

4.2 Penetration of Slurry Into Fiber Bundle

The Nicalon square weaves used in the infiltration experiments were woven from cylindrical Nicalon fiber bundles, or tows. Each tow consists of approximately 250 filaments/tow. The idealized system shown in figure 34 consists of a two dimensional weave with fiber tows in a square array. All tow/tow contacts are of an over-and-under type. The penetration of matrix silicon/cyclohexane slurry into a fiber bundle was modeled in terms of the capillary action driving the infiltration and the
Figure 34: Schematic representation of two-dimensional weave composed of fiber tows of diameter $2a$. 
viscous resistance to this fluid motion. The analysis developed here is similar to the work presented by Bohin et. al. (Bohin. 1994) modeling the penetration of silicone polymers into porous spherical silica agglomerates. Our analysis involves the penetration of a non-Newtonian fluid following the power law into a cylindrical tow of cylindrical Nicalon fibers. The area analyzed for slurry penetration represents a typical cross-section of the weave of fiber tows. From SEM micrographs we know that the size of the silicon particles penetrating the fiber tow is substantially less than the size of the interfiber gaps through which the fluid flows. As a result our model assumes the continuum description of the fluid is valid.

The pressure drop across banks of tubes is a familiar problem in heat exchanger design. The arrangement of the fibers in the fiber tow is analogous to a tubular heat exchanger. The pressure drop in the laminar flow regime (Re<100) of liquids across banks of fiber filaments for isothermal conditions is given by equation 25 (Perry. 1973):

\[ \Delta P = \frac{280 N_r}{Re_e} \left( \frac{D_t}{c} \right)^{1.8} \left( \frac{\rho v_{max}^2}{2g_c} \right) \]  (25)

where \( N_r \) is the number of fiber rows, \( D_t \) is the fiber diameter, \( \rho \) is the fluid density, \( g_c \) is the gravitational constant and \( v_{max} \) is the maximum fluid velocity through the minimum free flow area. For this analysis a staggered arrangement of the tubes as
Staggered Arrangement
Fiber Bank Configuration

Figure 35: Fiber tow configuration
shown in figure 35 is assumed to represent the arrangement of fibers within the fiber bundle of radius \(a\). For banks of staggered fibers \(c\) is the pitch as shown in figure 35 where \(c=1.25D_i\). The Reynolds number \(Re_c\) is defined as:

\[
Re_c = \left( \frac{D_i v_{\text{max}} \rho}{\mu} \right)
\]

(26)

where \(D_i\) is the volumetric hydraulic diameter (4× free bundle volume/exposed surface area of fibers). The non-Newtonian silicon slurry is again represented by the power law where:

\[
\tau = -m \left( \frac{\partial v}{\partial r} \right)^{-1/2} \left( \frac{\partial v}{\partial r} \right) = -\mu \left( \frac{\partial v}{\partial r} \right)
\]

(27)

and \(\mu\) is the apparent viscosity

\[
\mu = m \left( \frac{\partial v}{\partial r} \right)^{-1/2}
\]

(28)

for our purposes here we will substitute \(\frac{\partial v}{\partial r}\) with the maximum velocity between the fibers divided by half the spacing between the fibers i.e.

\[
\frac{\partial v}{\partial r} = \frac{v_{\text{max}}^2}{c - D_i}
\]

(29)

Equation 25 becomes

\[
\frac{\partial P}{\partial r} = \frac{280 N_r (D_i/c)^{10} v_{\text{max}} m (2v_{\text{max}})}{2 (c - D_i)}
\]

(30)

Hence, the velocity of the silicon slurry penetrating through the bed of fibers is:
\[ v_{\text{max}} = \left( \frac{\partial P}{\partial r} \right) \frac{2^{1/2} D_i^2 g_c}{140 N_m (c - D_i)^{1/2}} \left( \frac{c}{D_i} \right)^{1.5} \]  \text{(31)}

where \( \frac{\partial P}{\partial r} \) is the pressure gradient driving the flow. The volumetric flow rate, \( Q \), of a fluid into a fiber tow can be described by:

\[ Q = -2\pi r L v_{\text{max}} \]  \text{(32)}

where \( L \) is the length of the tow. Substituting the expression for \( v_{\text{max}} \) in equation 31. into equation 32 gives:

\[ Q = -2\pi r L \left( \frac{\partial P}{\partial r} \right) \frac{2^{1/2} D_i^2 g_c}{140 N_m (c - D_i)^{1/2}} \left( \frac{c}{D_i} \right)^{1.5} \]  \text{(33)}

Equation 33 can be used to calculate the pressure difference from the perimeter of the fiber tow to the penetrated layer in the tow:

\[ \int_{r_e}^{r_i} \frac{\partial P}{\partial r} = \left( \frac{-Q}{2\pi L} \right)^{1/2} \frac{140 N_m (c - D_i)^{1/2}}{2^{1/2} D_i^2 g_c} \left( \frac{D_i}{c} \right)^{1.5} \int_{u}^{r} \frac{\partial r}{r^{1/2}} \]  \text{(34)}

Integrating equation 34, the pressure difference is given by:

\[ P_R - P_u = \left( \frac{-Q}{2\pi L} \right)^{1/2} \frac{280 N_m (c - D_i)^{1/2}}{2^{1/2} D_i^2 g_c} \left( \frac{D_i}{c} \right)^{1.5} \left( R^{1/2} - u^{1/2} \right) \]  \text{(35)}

The pressure drop across the fluid-air interface due to surface tension for a two cylinder geometry can be calculated using (Carnali, 1993):

\[ P_m - P_R = \frac{2\gamma \cos(\theta + \alpha_m)}{c - D_i \cos \alpha_m} \]  \text{(36)}

where \( P_m \) is the air pressure in the interfiber gap, \( \theta \) is the contact angle and \( \gamma \) is the
Figure 36: Cross section through center of mesh showing liquid air meniscus which wets the fiber with contact angle $\theta$. 
fluid surface tension. A cross section through the center of one of the tows in the weave is shown in figure 36 in which the liquid-air meniscus is shown for a liquid wetting the fibers with contact angle $\theta$. The position of the meniscus relative to the fiber is given by the angle $\alpha_m$ defined as:

$$\alpha_m = \sin^{-1} \left( \frac{D_i \sin \theta}{c} \right) - \theta$$  \hspace{1cm} (37)

Adding equations 35 and 36 gives:

$$P_m - P_\alpha = \frac{2\gamma \cos(\theta + \alpha_m)}{c - D_i \cos \alpha_m} + \left( \frac{-Q}{2\pi L} \right) \frac{280 N_c m (c - D_i)^{1/2}}{2^{1/2} D_i^2 g_c} \left( \frac{D_i}{c} \right)^{16} (R^{1/2} - a^{1/2})$$  \hspace{1cm} (38)

Now considering that the air in an interfiber gap (capillary) is vented to the exterior of the fiber tow, $P_m = P_\alpha$. Equation 38 can be rearranged to give:

$$\left[ \frac{2^{1/2} \gamma \cos(\theta + \alpha_m) D_i^2 g_c}{140(c - D_i \cos \alpha_m) N_c m (c - D_i)^{1/2}} \left( \frac{c}{D_i} \right)^{16} \right] = \left( \frac{Q}{2\pi L} \right) (R^{1/2} - a^{1/2})^2$$  \hspace{1cm} (39)

The volumetric flow rate can also be written in terms of the advancement of the liquid-solid interface.

$$Q = -2\pi RL \frac{cR}{\alpha}$$  \hspace{1cm} (40)

Substituting equation 40 into equation 39 gives:

$$\left[ \frac{2^{1/2} \gamma \cos(\theta + \alpha_m) D_i^2 g_c}{140(c - D_i \cos \alpha_m) N_c m (c - D_i)^{1/2}} \left( \frac{c}{D_i} \right)^{16} \right] \frac{cR}{\alpha} = -R(R^{1/2} - a^{1/2})^2 cR$$  \hspace{1cm} (41)
Integrating equation 41 subject to the boundary condition that at \( t=0, \ R=a \) yields

\[
\left[ \frac{3\cdot 2^{1/2} \gamma \cos(\theta + \alpha_m) \Delta \gamma_{\text{c}}}{a^{3/2} 14(c - D_f \cos \alpha_m) N_r m(c - D_f) \gamma_{\text{c}}^2} \right] \frac{c}{D_f} \left[ \frac{3 \cdot 2^{1/2} \gamma \cos(\theta + \alpha_m) \Delta \gamma_{\text{c}}}{a^{3/2} 14(c - D_f \cos \alpha_m) N_r m(c - D_f) \gamma_{\text{c}}^2} \right] \frac{c}{D_f} = -10 \left( \frac{R}{a} \right)^3 + 24 \left( \frac{R}{a} \right)^{5/2} - 15 \left( \frac{R}{a} \right)^2 + 1 \quad (42)
\]

Equation 41 describes the kinetics of the process of silicon/cyclohexane slurry penetration into a tow of cylindrical fibers. Equation 42 can be rewritten in a simplified form as:

\[
\Lambda t = -10 \left( \frac{R}{a} \right)^3 + 24 \left( \frac{R}{a} \right)^{5/2} - 15 \left( \frac{R}{a} \right)^2 + 1 \quad (43)
\]

where: \( \Lambda = \left[ \frac{3\cdot 2^{1/2} \gamma \cos(\theta + \alpha_m) \Delta \gamma_{\text{c}}}{a^{3/2} 14(c - D_f \cos \alpha_m) N_r m(c - D_f) \gamma_{\text{c}}^2} \right] \frac{c}{D_f} \left[ \frac{3 \cdot 2^{1/2} \gamma \cos(\theta + \alpha_m) \Delta \gamma_{\text{c}}}{a^{3/2} 14(c - D_f \cos \alpha_m) N_r m(c - D_f) \gamma_{\text{c}}^2} \right] \frac{c}{D_f} \). The time for total penetration of the fiber tow, \( t=t_{\text{max}} \) corresponds to \( \left( \frac{R}{a} \right) = 0 \), where:

\[
t_{\text{max}} = \frac{1}{\Lambda}
\]

Figure 37 illustrates the observed kinetics of silicon/cyclohexane slurry penetration into a fiber tow. The figure shows the dimensionless penetration depth versus dimensionless penetration time. For \( \gamma=0.5 \times 10^{-2} \text{ Nm}^{-1}, \ \theta=8^\circ \) (Fisher. 1979). \( D_f=12 \ \mu \text{m}, \ c=15 \ \mu \text{m}, \ m=0.2 \ \text{Nm}^{-1}, \ \alpha=118 \ \mu \text{m}, \ D_r =6.76 \ \mu \text{m} \) and \( N_r =8 \) for 250 filaments/Nicalon tow, the maximum penetration time for this system is \( t/\Lambda \approx 0.01 \) s.

Hence, the penetration of the dispersion into the fiber weave is essentially instantaneous. This prediction agrees with the high quality infiltrations observed from the experimental fiber weave dippings.
Figure 37: Fiber tow dimensionless penetration time versus dimensionless fiber bundle radius.
5.0 CONCLUSIONS

The esterification of 1-octadecanol to the surface of the silicon powder gave the powder surface organophilic and hydrophobic characteristics demonstrated by particle size distribution analysis and sedimentation rate studies, allowing further processing to be performed in cyclohexane solvent. Adsorption studies showed that the C\textsubscript{18}H\textsubscript{37}O organic group provided an effective barrier to polystyrene adsorption, allowing the polystyrene to remain free in solution. The chemical grafting of the C\textsubscript{18}H\textsubscript{37}O organic group to the silicon surface additionally prevented any further oxidation of the silicon surface that could interfere in later nitridation processes. The presence of the C\textsubscript{18}H\textsubscript{37}O organic group effectively provided sufficient steric repulsion to balance the depletion flocculation forces, allowing utilization of both the slurry stability and the high solids loading resulting from the phase separation process. Examination under an electron microscope did not reveal any changes in the silicon powder after esterification, and indicated that only primary particles were participating in the esterification reaction. Thermal Gravimetric Analysis of a sample of 0.07 - 0.3 \( \mu \)m silicon-C\textsubscript{18}H\textsubscript{37}O showed that the C\textsubscript{18}H\textsubscript{37}O groups on the surface of the powder account for approximately 4 wt% of the esterified powder after 6 hours of reaction time at 200°C.

Phase separations were achieved with the esterified silicon-C\textsubscript{18}H\textsubscript{37}O powder in cyclohexane solvent using polystyrene with a molecular weight of 5780 as the free
non-adsorbing polymer. The stability of the lower phases resulting from phase separation varied as a function of the free polystyrene concentration as demonstrated by viscosity measurements, sediment height measurements and SEM micrographs. Hence the stability of the slurry could be externally controlled. Maximum slurry stability was achieved with a solids loading of approximately 40 wt% at a free polystyrene concentration $C_p \leq C \leq C_r$. The lower silicon rich phases were used to obtain coatings of silicon powder on SCS-6 fibers. The quality of the coatings was found to be dependent on the stability of the lower phase resulting from phase separation. Optimum coatings were achieved in the free polystyrene concentration range $C_p \leq C \leq C_r$. These coatings were uniformly distributed, closely packed with a low porosity and up to 6 μm thick. Particle shape and size also significantly affected the coating quality. The technique was effective for angular shaped primary particles and broad particle size distributions. However, more densely packed, lower porosity coatings could be obtained with more spherically shaped particles and smaller particle size distributions.

The colloidal phenomena of depletion stabilization/flocculation was also found to be an effective processing technique for fiber weave infiltration. The optimum single fiber coating conditions as determined by large diameter SCS-6 fiber dipping experiments was scaled up for small diameter fiber weave infiltration experiments. Infiltrated weaves were cold pressed, hot pressed and nitrided to enable
investigation of the infiltration quality via SEM examination of cross section samples of the infiltrated weave. SEM micrographs of infiltrated Nicalon square weaves showed a uniform infiltration of matrix powder throughout. A variety of other weaves were infiltrated to determine if the technique was also robust as to fiber type. Surface, shape, diameter and weave design. Nicalon silicon carbide fiber satin weaves, HPZ fiber satin weaves, Thornel carbon fibers in a twill weave style and Stackpole Panex WCG carbon fibers in a plain square weave were also infiltrated. All cross sections showed a high quality of infiltration with uniform distribution of matrix powder throughout.

The application of a non-Newtonian fluid onto a cylindrical fiber continuously withdrawn from a bath was analyzed. The fiber coating was determined to be a function of the fiber pulling speed, and the non-Newtonian fluid rheology as experimentally measured by the silicon lower phase viscosity studies. The fiber coating maximum thickness was determined for a range of withdrawal speeds. Higher withdrawal speeds resulted in thicker coatings. The experimentally measured fiber coating thicknesses were within the upper limits set by the fiber coating model.

The penetration time of silicon/cyclohexane slurry into a small diameter fiber bundle was modeled in terms of the capillary action driving the infiltration and the viscous forces resisting the penetration. Again the non-Newtonian rheological properties of the fluid were included in a packed fiber bundle pressure drop
correlation. The results of the analysis show that the penetration time begins very slowly, then proceed rapidly and then slows again at almost total penetration. The total penetration time is on the order of 0.01 s for the fiber bundles and silicon slurries used in the experimental studies. The short penetration times indicated that the capillary forces dominated the resistive forces and was confirmed by the experimentally observed high quality penetration of the fiber weaves.

The depletion stabilization technique utilized in the fiber weave infiltration process has several attractive features making it potentially useful for commercial scale processing. The lower phase slurries are thermodynamically stable which accommodates large batch scale operations taking several days to complete. The combination of high solids loadings and maximum interparticle stability resulting from the phase separation has been demonstrated to effectively and uniformly infiltrate fiber weaves. Some disadvantages of the technique are the additional processing steps (particle organic layer grafting reaction and the removal of excess organic particle coating) which increase overall processing costs and time. The technique requires the use of large amounts of narrow molecular weight distribution polystyrene which is expensive. The possibility of recycling the polystyrene exists since it is not consumed by the process, which could minimize these raw material costs. The technique is very dependent on the primary particle size and shape which was demonstrated by the significant change in fiber coating quality. Continuous monitoring of the particle size and shape would also be required due to the impact of
the change in the physical conditions necessary to induce a phase separation as a result of varying particle size.
The depletion stabilization/flocculation experiments performed in this work involve polystyrene free depletion polymer with a molecular weight of 5780. These high grade polymers are costly to produce in the narrow molecular weight ranges required for these studies. Additionally, large amounts of the polymer were required to initiate phase separation, further increasing costs. Several studies (de Hek 1979, Pathmamanoharan 1981) have shown that increasing the molecular weight of the free depletion polymer results in decreased free polymer concentrations required to induce phase separation. Hence the conditions of maximum slurry stability requiring less free polymer is more cost effective and potentially easier to recycle.

The experimental work in this study involved the chemical grafting of an organic layer onto the particle surface. The initial C_{18}H_{37}O-Si reaction apparatus and phase separation process used for fiber dipping was scaled up to accommodate the larger weaves for infiltration studies. Due to the severe temperature and pressure conditions required to remove the excess C_{18}H_{37}OH after the grafting reaction, the process was difficult to control and required continuous monitoring. Iler has successfully chemically grafted a variety of shorter chain alcohols to the surface of silica particles produced via the Stober process (Iler, 1961). Similar chemical grafting of shorter chain alcohols onto milled silicon particles could provide several advantages to the process. The use of a shorter chained hydrocarbon for the required
steric and adsorption roles would simplify the excess post reaction hydrocarbon removal process. Additionally, shorter chained hydrocarbons would result in decreased organic additives which are removed in the binder burnout stage prior to nitridation, potentially improving the overall quality of the nitrided composite.

The strength of the dispersant-particle interaction can be enhanced by establishing a chemical bond between the stabilizing molecule and the particle such as the C_{18}H_{37}O-Si reaction utilized in this work. Both short and long chain stabilizing molecules have been attached to various ceramic particles (Green. 1987). This technique replaces the relatively weak interaction associated with adsorption. the mechanism of traditional steric stabilization techniques. Establishing a strongly bound organic layer that resists desorption should prove advantageous in ceramic processing for a variety of reasons: improvement in colloidal stability, better process control and increased processing flexibility. Adsorption and desorption are complicated phenomena reliant on system variables such as dispersant and particle concentration and solvent character. For ceramic systems which typically contain many components and often involve extreme changes in conditions during processing, chemical bonding of the dispersant to the particles may be more reliable than adsorption. Studies of these mechanism however are in their infancy.

Chemical bonds between stabilizing molecules and particle surfaces have been achieved with other powders: Al_{2}O_{3}, BaTiO_{3}, and SiC (Green. 1987). The feasibility
of involving other ceramic particles in similar depletion stabilization/flocculation studies has not been investigated. The use of Al$_2$O$_3$ and BaTiO$_3$ for example could result in fiber coatings for sapphire fibers and weaves.

The maximum lower phase slurry solids loading achieved in this work was approximately 40 wt%. Examination of the effect of solids loading on the slurry rheology and overall infiltration quality may lead to an optimized infiltration process and improved composites.

Fiber coating provides a means of controlling the nature of the fiber-matrix interface in composite materials to ensure that toughness and strength are maintained at high temperatures. A number of commercially available ceramic fibers are coated by a variety of techniques such as chemical vapor deposition, sol-gel, and polymer pre-cursor methods. The coating of fibers in the past by colloidal slurry processing techniques utilizing the surface charge on the fibers and particles (Malghan. 1990) have yielded non uniform and porous coatings. The SEM micrographs in this work show that fiber coatings with controllable, uniform, low porosity coatings can be achieved using depletion slurry processing techniques. An investigation into the mechanical properties of these single fiber coatings may yield a simple, low cost alternative fiber coating process.
This work did not involve the mechanical testing of the nitrided composites. The overall mechanical properties of the fiber reinforced composites are significantly affected by the quality of the weave infiltration. Further investigation of the effects of the infiltration extent are needed to quantify the improved composite quality as a result of the colloidal processing techniques.

The infiltration technique used in this work was exclusively via the simple vertical dip method. The ease of infiltration and robustness of the technique could be further improved by the use of other infiltration techniques, such as with the use of high pressure or a tape casting type technique. The infiltration of more complex three dimensional weaves has not been attempted. If such composites can be infiltrated via depletion routes, a class of fiber reinforced ceramic matrix composites with unique mechanical properties may result.


