Mechanical and Physical Properties
of
Particulate Reinforced Composites
by
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Thesis submitted to the faculty of
the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Master of Science
in
Materials Science and Engineering

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November, 1993
Blacksburg, Virginia
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(ABSTRACT)

The effect of particle size matching and mismatching on the processability, and the mechanical and physical properties of particulate reinforced composites is investigated in this study. These composites were made from dry powder-powder blends. Polymer and reinforcement materials were chosen, characterized and molded into composite plaques. For the same particle volume fraction (40%), stiffness was found to increase, in general, as particle size decreased. The intimacy of mixing, stiffness and strength improvements depended upon the reinforcement type. These results were compared with predictions from simple micromechanics models to gain a better understanding of their physical behavior.
Acknowledgements

I would like to extend thanks to my advisor, Dr. Ronald G. Kander, for his constant support and encouragement over the course of this study. I would also like to thank Dr. Ronald D. Kriz and Dr. Stephen L. Kampe for agreeing to serve as members of my committee. My work on this project would not have been possible without the funding I received from the NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites (#DMR 912004), and I would like to extend my appreciation for their support.

In conducting the experimental work for this project, I received assistance from many knowledgeable and extremely helpful people. I would like to thank and recognize the assistance of: Gene Li, for his assistance in performing the adsorption experiments; Dr. Dillard's group, for assistance with flexural tests; Mr. Mac McCord, for assistance with particle size analysis, C-scan measurements, acoustic microscopy work, and velocity measurements; Andy Brink, for assistance with the adsorption technique; Mike Farrell, for assistance with DSC work; Dr. Kriz and Mike Butsch, for their assistance with the scientific visual analysis computers; Hélène Cornélis, for assistance with scanning electron microscopy and DSC work; and Shannon Namboodrī, for assistance with scanning electron microscopy work, and composite fabrication.

I would like to thank my fellow 'groupies' for their constant friendship and support: Hélène Cornélis, Shannon Namboodrī, Joel Lee, Linda Vick, Rick Clark, Mike Farrell, and Ravi Verma. Special thanks goes out to Hélène, Shannon, and Linda for their friendship, and understanding, which mean a great deal to me.

I would like to thank my parents, Kenneth and Carol Reed, and my entire family, for their continual love and support. And finally, the most deeply felt thanks are extended to my husband, Michael Butsch, for his support, love and infinite patience.
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1 Introduction

"The principles of polymer reinforcement with dispersed fillers at low and high strain are not yet quite clear. While the addition of ultra fine-dispersed carbon black and silica to elastomers results in an almost all-round improvement of properties, it has so far been impossible to obtain a similar effect in plastics."


Successful injection molding of a dispersion filled thermoplastic (traditionally 10-15% rigid filler) may only be attained by carefully and accurately controlling the temperature and using the highest possible injection pressure. Current technology allows filled thermoplastics (40% filler), with improved properties, to be processed by a dry powder-powder compression molding technique. With this technique, successful fabrication of a dispersion filled thermoplastic was attained in this study by monitoring the processing temperature, and using moderate pressures.
Particulate fillers are most commonly used in polymers as low volume fraction dispersed fillers. These filled polymers can be described as a soft, continuous phase (the polymer phase) with hard, discontinuous fillers. The advantages of fillers on the modulus of a polymeric composite system can be better understood by considering three specific examples: injection molded parts, elastomers and engineering thermoplastics.

**Injection molded parts**

Acting as miniature ball bearings to improve flow in the injection molding process, the use of fillers with a spherical shape lowers the energy required to melt mix most resin systems, which results in low resin usage, fewer defects due to poor flow, low mold shrinkage and low product warpage. High loading can increase flexural modulus and improve stress distribution, leading to better finished products. The isotropic nature of spheres allows for better filler packing, produces a more uniform shrinkage rate throughout the part and results in improved manufacturing quality.\(^2\)

**Elastomers**

Styrene-butadiene rubber (SBR) is an example of a filled elastomer. The addition of rigid filler particles results in an increase of the modulus of elasticity (stiffness). When subjected to a tensile load at an elevated temperature, a filled elastomer (such as SBR) experiences an increase in elongation because the material has become less sensitive to flaws. This decrease in sensitivity due to the filler increases the crack propagation path length. The dispersed particles adsorb a portion of the energy available to grow the crack. Therefore, in a filled system, more energy is adsorbed by the material before a crack reaches its critical failure length.\(^1\)
Engineering Thermoplastics

At normal temperatures, brittle failure of filled thermoplastics is observed with filling ratios of 10-15 vol%. During deformation of the composite, voids are formed at the interface when the matrix becomes detached from the filler particles. The void size is determined by the filler particle size -- the smaller the particle, the smaller the resulting void due to dewetting of the matrix material. The stress at which the void begins to grow is related to the filler particle size by a Griffith-type equation: \( \sigma \sim \frac{1}{\sqrt{p}} \) where \( p \) is the maximum void size, about equal to the particle size. Consequently, to attain the maximum strength of a particulate filled polymer composite it would be desirable to use finely dispersed fillers that do not contain any large particles.\(^1\)

Advantages of Fillers on the Elastic Modulus

In a composite system, the overall modulus is intermediate between the high and low modulus components (the filler and matrix materials respectively). Increased stiffness is expected for a composite system that has a soft, continuous phase, with hard, discontinuous fillers. An example of a composite system in which the fillers increase the stiffness of the material is an elastomer with hard disperse fillers, such as styrene-butadiene rubber (SBR) with glass beads. Increased toughness is expected for a composite system that has a hard, continuous phase with soft, discontinuous fillers. An example of a composite system in which the fillers increase the toughness of the material is a discontinuous elastomeric filler that could be used with a ceramic matrix.

In this study, the matrix material is poly (ether-ether-ketone), PEEK, and the filler material is either a metal or a ceramic. This composite system lies between the two extremes described above.

There have been many published papers on the calculation of the elastic moduli of composite materials with spherical inclusions. Differential models exist to calculate the elastic moduli of a solid that contains a random distribution of spherical inclusions, and
closed-form solutions have been obtained for rigid inclusions and vacuous pores.\textsuperscript{3,4}

The Hashin-Shtrikman Expressions and the Rule-of-Mixtures/Inverse Rule-of-Mixtures are the methods of predicting the elastic modulus for composite materials that were used in this study. These predictive equations are based on the component volume fraction and elastic modulus, and do not take the filler shape into account.

The lower bound of the Hashin-Shtrikman Expressions describes the case of a soft, continuous matrix with a disperse hard phase. The upper bound describes a hard, continuous matrix with a disperse soft phase:

**Hashin-Shtrikman Expressions**

**Lower Bound:**

\[ K_L = K_m + V_r \left[ \frac{1}{(K_r - K_m)} + 3(1 - V_r)/(3K_m + 4G_m) \right] \]

**Upper Bound:**

\[ K_U = K_r + V_m \left[ \frac{1}{(K_m - K_r)} + 3(V_r)/(3K_r + 4G_r) \right] \]

*where*

- \( K = \) Bulk Modulus = \( E / (3(1-2v)) \)
- \( G = \) Shear Modulus = \( E / (2(1+v)) \)
- \( E = \) Elastic Modulus = \( 4KG / (3K+G) \)
- \( v = \) Possion's Ratio

**Voigt-Reuss Bounds**

**Lower Bound (Inverse Rule-of-Mixtures):**

\[ \frac{1}{E_L} = \frac{V_r}{E_r} + \frac{V_m}{E_m} \]

**Upper Bound (Rule-of-Mixtures):**

\[ E_U = V_r E_r + V_m E_m \]
The Voigt-Reuss Bounds are more commonly known as Rule-of-Mixtures and Inverse Rule-of-Mixtures (derived in Chapter 5.1). The upper and lower bounds for the Voigt-Reuss Bounds correspond to the same physical conditions as the Hashin-Shtrikman Expressions. A material described by the upper bounds experiences a state of isostrain; whereas, a material described by the lower bounds experiences isostress (described in more detail in Chapter 5.1). The Hashin-Shtrikman Expressions give conservative modulus values; consequently, the Voigt-Reuss Bounds are more often used. 5

Many theories on the stiffening of a filled rubber have been derived from Einstein's equation for the viscosity, \( \eta_c \), of a dilute suspension containing a low volume fraction (10-15%), \( v_f \), of equal diameter rigid spherical particles in a liquid of viscosity, \( \eta_m \):

\[
\eta_c = \eta_m \times (1+2.5v_f)
\]

where the subscript c denotes the composite, and m the matrix.6 The relationship of viscosity to volume fraction is identical to the relationship for the modulus of a low volume fraction dispersion of completely rigid spheres in a rubber matrix6:

\[
E_c = E_m \times (1+2.5v_f) \quad (a)
\]

This expression was expanded to account for not only the aspect ratio, \( f \), of the filler, but also higher filler volume fractions6:

\[
E_c = E_m \times (1+2.5fv_f + 1.62f^2v_f^2)
\]

For the case of fillers with spherical shape (aspect ratio of 1), this becomes6:

\[
E_c = E_m \times (1+2.5v_f + 1.62v_f^2). \quad (b)
\]
Expressions \( a \) and \( b \) approach one another at low filler volume fractions (\(<-10\%)\). However, as the filler volume fraction increases, the composite modulus values calculated by \( a \) and \( b \) begin to diverge.

Lewis and Nielsen\(^7\) applied the above relationship for Young's modulus (\( a \)) to shear modulus:

\[
G_c = G_m \times (1 + 2.5v_f)
\]

then related shear modulus to viscosity by the relative modulus:

\[
G_r' = \left( \frac{G_c}{G_m} \right) = (1 + 2.5v_f)
\]

In their research, Lewis and Nielsen studied the effect of filler particle size and volume fraction for an epoxy/soda lime glass bead system. The particle size ranges of the glass beads used in their research were 5-10 \( \mu \)m, 10-20 \( \mu \)m, 30-40 \( \mu \)m, and 75-90 \( \mu \)m. The volume fraction was varied from 0 to 0.40.

As seen in Figure 1, their results indicate that for a fixed volume fraction, as particle size decreases, the relative modulus of the system (\( G_r \)) increases.

A logical question to ask at this point is why the concern over particle size? The particle size of the filler and matrix powders plays a role in the microstructural dispersion of the composite, as seen in Figure 2a - 2c. In general, it was observed in our study that more intimate mixes were obtained with finer matrix and filler powders. However, the ease of processing the composite was not necessarily increased with the more intimately mixed powders. To better understand, let's examine the effects of small, spherical particulate reinforcement and matrix materials.

Small, spherical particulate reinforcements may have an advantage over larger, spherical particulate reinforcements in that there is an increased surface area-to-volume ratio which means
**Figure 1:** Relative Modulus vs. Volume Fraction Filler for an Epoxy /Soda Lime Glass Bead System
Figure 2-a: Matched matrix and filler particle sizes
(matrix/filler ratio = 1)

Figure 2-b: Matrix particles smaller than filler particles
(matrix/filler ratio < 1)

Figure 2-c: Matrix particles larger than filler particles
(matrix/filler ratio > 1)
(dark = matrix, light = filler)
that there is more interface for a fixed volume fraction of filler. As the amount of interface present increases, the crack path becomes more tortuous; consequently, the amount of energy adsorbed by the composite should increase. Increasing the amount of interface present may also modify the matrix properties because the matrix polymer has more chains in contact with the filler particle surface. Finally, smaller, spherical filler particles are more uniformly distributed. If the particles are close enough together that all of the effective matrix is interface, then a two component material (filler & interface), not a three component material (filler, interface & matrix) could result.9

Small particulate matrix materials, in general, produce a more intimately mixed blend. Since the polymer matrix material in question is a particulate, the powder metallurgical idea of sintering of particles can be applied. For a given testing temperature, the diffusion rate is a function of the particle's surface area. Smaller particles have an increase in surface area which allows for sintering of the polymer at either lower temperatures or shorter times. Finally, polymers at the submicron level have many chains in contact with the surface of the filler material, which increases the mobility of the chain and is thought to decrease the effective Tg of the polymer. Decreasing the effective Tg would increase the ease of processing the material, since the polymer would not require as much energy to flow.9

The relative particle sizes of the matrix and filler powders have a great effect on the homogeneity of the particulate composite. For matched particle sizes, a uniform microstructure would result, see Figure 2-a. If the matrix particles are smaller than the filler, then a uniform microstructure could form (see Figure 2-b). When the matrix particles are larger than the filler, there is an increased tendency to produce microstructures having regions containing filler agglomerates and regions containing only matrix material, see Figure 2-c.10
In this thesis, particulate reinforced composites are made from a dry powder-powder blend compression molding process. For a fixed volume fraction, the matrix and filler particle sizes are matched and mismatched to determine the effect of particle size on the mechanical and physical properties of the resulting composite. The constituent materials were characterized, fabricated into composites and the composite's properties are compared with simple theoretical models of particulate reinforced composites. In Chapter 2, the materials used in this work are described. In Chapter 3, details of particle size separation, particle size characterization, the fabrication process used in making the composites, techniques used to characterize the composites, and a process to adsorb polymer onto the filler to improve processing are described. In Chapter 4, characteristics of the dry powder-powder blend compression molding technique are reviewed, the mechanical and physical behavior of the composites materials are discussed, and attributes of the adsorption technique are described. In Chapter 5, the behavior of the materials made in this study are compared to predictions made through simple micromechanics modeling of the material systems. In Chapter 6, the work of this thesis is summarized, the importance is discussed, potential applications are addressed, and future work is proposed.
2. Materials

2.1 Polymer Matrix Materials

2.1.1 Poly (aryl ether ether ketone)

'Vicrlex' PEEK is a high temperature, semicrystalline, thermoplastic polymer manufactured commercially by ICI. The chemical structure of PEEK is shown in Figure 3. The PEEK powder used in this study was commercial powder supplied by ICI, grade 150 PG. This powder was separated into the following particle size ranges (separation method described in Chapter 3.1): greater than 106 μm, 106+90 μm, 90+75 μm, 75+53 μm, 53+45 μm, 45+38 μm, 38+25 μm, and less than 25 μm. The particle size ranges that were used in the fabrication process include greater than 106 μm, 75+53 μm, 45+38 μm, and less than 25 μm (the notation XX+YY means that YY μm < particle's size μm < XX μm).

According to the ICI literature, the bulk PEEK powder melts at 340°C, undergoes a glass transition at 143°C, has a number average molecular weight of 16,000 and a weight average molecular weight of 32,000. The molecular weight values reported by ICI were determined by calculations based on the melt viscosity of PEEK. The molecular weights of PEEK have not been directly verified on campus because of the inability to perform the appropriate intrinsic viscosity measurements.
After the PEEK powder was separated into the various particle size ranges (as will be discussed in Chapter 3.1), the powder was further characterized in terms of size and shape. In addition, differential scanning calorimetry was used to characterize the PEEK powder. Figure 4 shows DSC results for the various PEEK powder particle size ranges used in this study. An indication of the size and shape of the PEEK particles is shown in Figure 5.

\[ \text{Figure 3: Chemical Structure of PEEK.} \]
Figure 4: A typical DSC scan of PEEK particle size ranges used in this study.
Figure 5: A typical micrograph of PEEK.
2.1.2 Poly (pyridine ether -co- ether ether ketimine)

The structure of Poly (pyridine ether -co- ether ether ketimine)\textsuperscript{11} is shown in Figure 6. An indication of the size and shape of Poly (pyridine ether -co- ether ether ketimine) is shown by an optical micrograph in Figure 7. This random copolymer is comprised of 20% pyridine-t-ketimine and 80% ether-ether-ketimine. The number average molecular weight was determined by GPC (gel permeation chromatography) to be 32,900, the weight average molecular weight was 62,000.

![Chemical Structure Image]

\textbf{Figure 6:} The structure of random Poly (pyridine ether -co- ether ether ketimine).
Figure 7: An indication of the size and shape of Poly (pyridine ether -co- ether ether ketimine).
2.2 Reinforcement Materials

Spherical particulates (metal or ceramic) were used as reinforcements. The primary gain expected from these reinforcements is increased stiffness.

2.2.1 Copper

Copper is one of the earliest known metals. Copper is reddish, lustrous, ductile and malleable; face-centered cubic in structure; and commercially available in the form of ingots, sheets, wire or powder. Manufactured in the form of bronze, brass, and other alloys, copper derivatives are commonly used in electrical conductors, ammunition, copper salts and works of art. The copper used in this study was in the form of powders, these individual particles have distinctly spherical shape. This spherical shape is a result of the way in which the powder was processed -- gas atomization. Copper melts at 1083 °C, and is therefore thermally stable in the temperature range required to mold the composites in this study. The powder was supplied by United States Bronze Powders, Inc. This powder was reported to be 99% pure.

Figure 8 shows the X-ray pattern obtained which confirms the purity of the copper powder.

As will be discussed in Chapter 3.1, this powder was separated into the following particle size ranges: greater than 106 μm, 106+90 μm, 90+75 μm, 75+53 μm, 53+45 μm, 45+38 μm, 38+25 μm, and less than 25 μm. Of these ranges, the particle size ranges that were used in the fabrication process include greater than 106 μm, 45+38 μm, and less than 25 μm. A typical micrograph of the copper powders used is shown in Figure 9, illustrating the spherical nature of the powder.
Figure 8: X-ray pattern of Copper greater than 106 microns.
The copper reinforcements were the main filler materials that were used in this study. The silica powders were utilized in determining the best mixing methods for the powder blends, and in the experiments with the pyridine-PEEK copolymer. The mechanical and physical properties of the PEEK/hollow carbon sphere blends were examined; however, these blends were not the main focus of this research.

2.2.2 Hydrated (Fused) Silica

Computer memory chips, sand and glass all have at least one thing in common - silica. When used as fillers in composites, solid glass spheres enhance processing and reduce manufacturing costs. The use of solid glass spheres is well known in the plastics industry. They provide excellent melt flow and directional stability resulting in low resin usage, few defects due to poor flow, low mold shrinkage as well as low product warpage.2 Hydrated, amorphous, solid silica, commonly known as soda-lime glass, is one of the many forms of silica that exist. It is the form of silica used in this study. The powders (SphericeIR Type A 2429 Solid Glass Spheres, and SphericeIR Type A 3000 Solid Glass Spheres) were supplied by Potters Industries in particle size ranges of 95 μm and less than 25 μm, respectively. The softening point of the hollow glass spheres is 704°C, and is therefore thermally stable in the temperature range required to mold the composites made in this study. PPG Industries supplied 250 Angstrom hydroxylated silica. These materials were used as received. A typical micrograph of the silica used in this study can be seen in Figures 10 &11.

2.2.3 Fumed Silica

Fumed silica differs from fused silica only in that the silanol surface is coated with methyl groups, rather than hydroxyl groups. Aldrich supplied the fumed silica (<38 μm, 1-5 μm, 0.14 μm).
2.2.4 Hollow Silica

Hollow glass spheres displace the same volume as solid spheres of the same size; however, due to a hollow glass sphere specific gravity of 1.1 (most mineral fillers have a specific gravity of 2.4-2.9) the weight of the finished engineering plastic compound or molded part is significantly reduced. SphericelR 110P8 Hollow Glass Spheres provide the same benefits as conventional solid glass spheres, these boro-silicate spheres have an average particle size of 8 μm. The softening point of the hollow glass spheres is 704°C, and is therefore thermally stable in the temperature range required to mold the composites in this study. The micrograph seen in Figure 12 shows these hollow particles.14

2.2.5 Hollow Carbon Spheres

Carbon's unique properties such as chemical inertness, high temperature capability, low coefficient of thermal expansion and electrical conductivity make it a desired structural material - carbon fibers are the material of choice for fiber reinforced composites. Carbospheres, Inc. manufactures carbon in particulate form. With a specific gravity of 0.4, carbon reinforcements in the form of hollow, thin-walled spheres are used in this study to create an extremely light weight composite. The micrograph seen in Figure 13 shows these hollow carbon spheres.15
Figure 9: A typical micrograph of copper.
Figure 10: A typical micrograph of solid silica.

Figure 11: A micrograph of solid silica 250 Angstroms.
**Figure 12:** A micrograph of hollow silica, approximately 10 microns.
Figure 13: A micrograph of hollow carbon spheres, approximately 20 microns.
3 EXPERIMENTAL

3.1 PARTICLE SIZE SEPARATION

Since the focus of this research is on the effect of particle size matching and mismatching, the bulk PEEK and copper powders were separated into the following particle size ranges: greater than 106 $\mu$m, 106+90 $\mu$m, 90+75 $\mu$m, 75+53 $\mu$m, 53+45 $\mu$m, 45+38 $\mu$m, 38+25 $\mu$m, and less than 25 $\mu$m.16

3.1.1 Traditional (Wet) Sieving

Wet sieving is the traditional method of separating materials in the mining industry. This method requires the use of Tyler sieves #140 (106 $\mu$m), #170 (90 $\mu$m), #200 (75 $\mu$m), #270 (53 $\mu$m), #325 (45 $\mu$m), #400 (38 $\mu$m) and #500 (25 $\mu$m). The sieves are stacked with the smallest sieve number (largest mesh) on top, with a bucket on the bottom, see Figure 14. A fine mist of water is used to flush a small amount of powder through the top sieve. This process is repeated for all sieves. After all sieves have been flushed, the bucket contents are filtered. The filtrate is collected on filter paper, and dried in an oven overnight at 60°C.

25
Figure 14: An illustration of the sieving process.
3.1.2 Sonic Sieving

Copper and PEEK powders were wet sieved for all particle size ranges. The copper powder that was less than 25 microns was then sieved using an ATM Sonic Sifter, see Figure 15. The sonic sieve allowed the copper to be further separated into the following ranges: greater than 30 μm, 30+20 μm, 20+10 μm, 10+5 μm, and less than 5 μm. Due to PEEK’s low density (1.3 g/cc), the polymer was not able to be further separated by the sonic sieve.

Figure 15: The sonic sifter.
3.2 PARTICLE SIZE ANALYSIS

Several different methods of particle size analysis were performed. The first method involved placing the particles in a solution, suspending the particles (which proved to be challenging), then performing a particle size analysis. This analysis technique required that a suspension of particles in the electrolyte be drawn through the orifice which passed an electric current. Each particle in traversing the orifice, caused a momentary resistance change proportional to the particle volume. The resultant sequence of electric particle-pulses was then amplified, scaled and counted to yield particle count and size distribution data.\textsuperscript{17} The second method made use of the scanning electron microscope. This method was not rigorously pursued because of the difficulty in obtaining a statistically meaningful number of measurements per sample particle size. The final method incorporated the use of an image analysis system, as well as an optical microscope. This method proved to be the most accurate.

3.2.1 Electrolytic Solution

This method incorporated the use of an Elzone 80 xy analyzer and monitor. A solution of 150 ml of sodium pyrophosphate and 2-3 drops of Lomar D (a dispersant) was used to suspend the powders. The powders were placed in this solution, agitated for 30 seconds and then analyzed as described above. This method proved ineffective in the determination of the particle sizes of PEEK and Copper. However, it was adequate for the silica powders. Copper was too dense, $\rho = 8.96$ g/cc - - the particles would not stay suspended for the proper amount of time. The PEEK powders were not dense enough (1.3 g/cc); as a result, the powders floated on the surface of the solution. With a density of 2.46-2.49 g/cc, the silica powders were able to be suspended for a long enough period of time.
3.2.2 Image Analysis using Optical Microscopy

The most effective means of particle size analysis for all materials was using the image analysis equipment in the Non-Destructive Evaluation (NDE) laboratory. Loose powders were placed on a microscope slide. The microscope slide was then placed on an optical microscope. This microscope was interfaced with a computer with mouse driven software. The image from the optical microscope appeared on the computer screen. One could 'click' the mouse on one side of the particle, and 'drag' it to the other side. As seen in Figure 16, one measurement was taken per particle. For PEEK, which is an irregularly shaped particle, it was necessary to take the measurement along the longest axis of the particle. All filler particles were spherical in shape; consequently, the measurement could be taken in any direction. One hundred individual particle measurements were obtained for each material type and particle size range used in this study. The average particle sizes and standard deviations were recorded. For the hydroxylated and fumed solid silica the average particle sizes were indicated by the manufacturer.
**Figure 16:** A particle size analysis micrograph from the image analysis optical microscope.
3.2.3 Particle Characterization

The PEEK matrix powder used in this study contains irregularly shaped particles which were divided into several different particle size ranges. The following ranges were used to make the comparison of the effect of matrix particle size: greater than 106 μm, 75+53 μm, 45+38 μm and less than 25 μm. Differential scanning calorimetry (DSC) was used to characterize the glass transition temperature (Tg), the crystallization temperature (Tc) and the melt temperature (Tm) of the following PEEK particle sizes: 120 μm, 43 μm & 22 μm. These results will be discussed in Chapter 4.

The fillers used in this study were spherical in shape. These fillers were divided into several different particle size ranges: greater than 106 μm, 75+53 μm, 45+38 μm and less than 25 μm. Since these fillers are spherical, they have an aspect ratio equal to 1. This is important for the modeling of a particulate reinforced composite.

These particle size ranges were used to study the effect of varying filler and matrix particle sizes on the composite's behavior.

3.3 FABRICATION OF COMPOSITES

The composite samples were fabricated using a new technique of dry powder-powder compression molding. In this process, the 40 vol % filler and 60 vol % matrix powders were used to make the samples. Using the volume fraction and densities, weight fractions were determined for each component. The components were then weighed, blended, placed in the mold, and hot pressed using various pressing times and temperatures based on the size of the particles in the mix (discussed in section 3.3.2).

3.3.1 Blending

In forming a homogeneous, isotropic composite it is essential that the components be well mixed. Two methods of blending proportional amounts of the powders were used: hand mixing and mechanically mixing. The first mixing technique was the hand mixing method. This method required that the powders be weighed
out and placed in a vial. This vial was then rigorously shaken by hand in all three directions for thirty seconds. In the second mixing technique, the powders were placed in a vial and mechanically shaken for 5 minutes in a rigorous "figure 8" fashion in a SPEX R mill.

In order to achieve more intimate mixing of the PEEK and copper than is possible by mixing for 5 minutes, a technique that was explored for this powder blend is to actually mill the copper and PEEK particles together. For this study, both the copper and PEEK are of the same particle size range (greater than 106 microns). The volume percents of copper (40 vol %) and PEEK (60 vol %) are kept constant. The appropriate amount of powder is weighed out, placed in a SPEX R tungsten carbide vial and milled for 4, 6, or 8 hours with two 7/16" tungsten carbide balls, see Figures 17 & 18. The particle size of the polymer was altered as a result of the milling process. However, the 'new' average polymer particle size and distribution was not determined in this study.

3.3.2 Compression Molding of Dry Powder-Powder Blends

Compression molding of dry powder-powder blends is possible only when all of the components of the composite system are available as fine powders. With particles on the order of 20 microns in size, intimate mixing in the dry state is easier than when the particles are on the order of 100 microns in size. Mixing of the polymer and reinforcements in this study was achieved using the methods described above. The level of intimacy of mixing was determined by visual observation, and verified by C-scan and acoustic microscopy.

Once the powders are mixed, consolidation is a simple process. The blended powder was placed in a 4"x4" mold. This mold was then placed in a hot press and 3000 - 5000 pounds load (187.5 -312.5 psi) was applied. The contact pressure varied as the polymer and reinforcement powder sizes varied. For the case of large polymer and reinforcement sizes, 3000 lb applied load (187.5 psi) was required to stabilize the load. For smaller reinforcements, applied.
Figure 17: The SPEX mill used in the blending of powders.

Figure 18: The vials used in the blending of the powders.
loads of 4000 - 5000 lb (250 - 312.5 psi) were required. For smaller polymer sizes, nominal pressure was applied until the powder temperature exceeded the polymer's Tg (bulk powder Tg is 143°C), then a load was applied and maintained at 3500 - 4000 pounds (218.75 - 250 psi). In order to monitor the powder's temperature, a thermocouple was placed through the mold. The large particle size polymer blends were taken to 340°C at nominal heating rate of 10°C/min, held for approximately 10 minutes, then allowed to cool. For the smaller particle size polymer blends, the powder's temperature was taken to 320°C, held for 10 minutes, then taken to 340°C. This was done to ensure that the polymer had flowed. Once the platen temperature was air cooled to 300°F, the platens were then water cooled to room temperature. The mold was taken from the press, and the sample was released.

3.3.3 Sample Dimensions
Initially, samples were made to be 4"x4"x1/16". These specimens were then machined to be 2"x1/2"x1/16". The machined samples were used for the characterization of the composites.

3.4 CHARACTERIZATION OF COMPOSITES
Both mechanical and physical properties of the composites were studied.

3.4.1 Mechanical Properties
Mechanical properties were measured in order to determine the ability of the materials to withstand stress. Flexure, ultrasonic velocity measurements, tensile and impact tests were performed, and fracture surfaces were examined to determine failure modes.

Three-point-bend tests were performed on an Instron 4505, running with LabView software, to determine modulus, yield strength, and strain-at-failure. Tests were run using a load range up to 78N on a 1000 N load cell. A span to depth ratio of 16 was used for all samples. To adhere to ASTM method D 790-90, a
cross-head rate of 0.8 mm/min was used. Load and displacement were explicitly measured and converted to flexural stresses, strains, and moduli using linear beam theory and Labview™ software. The resulting stress/strain curves provide information on the ductility/brittleness of the composites. The following expressions show the sample dimension relationship to load and displacement used in three-point-bend theory:

\[ \sigma = (3/2) \cdot (s/w) \cdot (P/l^2) \]
\[ \epsilon = 6 \cdot (t/s^2) \cdot D \]
\[ E = (1/4) \cdot (s^3/wt^3) \cdot (P/D) \]

where \( s \) is the span, \( t \) is the sample thickness, \( w \) is the sample width, \( P \) is the applied load and \( D \) is the sample deflection.  

A quantitative measure of toughness was obtained by instrumented impact testing. Unnotched impact tests were performed on a Tinius-Olsen Charpy Impact Machine instrumented with a Dynatup load cell. In these tests, toughness was defined as the energy adsorbed during fracture, and was determined by measuring the integrated area under the load vs. time curve during impact.

Scanning electron microscopy (SEM) was performed on an ISI (model SX40) scanning electron microscope. This technique was used to examine the fracture surfaces of failed specimens to learn more about the mode of failure.

Optical microscopy tests were performed on the bulk powders prior to processing. This work was performed on an Olympus photomicroscope (model BH-2). Samples were examined in reflected light, in both bright and dark field, using polarized and non-polarized light. The image analysis studies were performed on an Olympus photomicroscope (model Cue2).
An Olympus acoustic microscope (model UH 3) was used to determine surface characteristics and mixing of the as molded composite surfaces.

Ultrasonic C-Scan tests were performed to determine sample homogeneity. These tests were run on an Automation Industries C-Scan (model S 80). Two transducers were used: a 2.25 MHz transducer, with a 3" focal length and a 1.25" element diameter and a 2.25 MHz transducer, with a 1.125" focal length and a 3.0" element diameter. These samples were run with the gain ranging from 40 to 70 dB, with applied frequencies ranging from 2.25 to 10 MHz.

Young's modulus, shear modulus, bulk modulus, and Poisson's ratio were determined for the copper filled PEEK samples by following the standard practice for measuring ultrasonic velocity in materials, ASTM E494. This method incorporates the use of a transmitter (pulser), a receiver (echo amplifier), and an oscilloscope. Since the samples used in this study are thinner than required by the ASTM method, two 2.25 MHz transducer were used (one acts as a transmitter, the other as a receiver). The sample was placed between the two transducers, and a pulse sent through the sample. Two back echo's were noticed: a longitudinal and a transverse wave. The primary back echo was used for determining the one-way travel time of the signal in both directions. The travel time was recorded for both directions. This time was divided by the sample thickness to derive the longitudinal and transverse velocities. These velocities were used with the theoretical density of the material to determine Young's modulus, shear modulus, bulk modulus, and Poisson's ratio. The equations used to calculate these values were taken from the ASTM 494 method, and, are as follows:

Poisson’s ratio: \[ \nu = \frac{[1-4(v_s/v_l)]/2[1- (v_s/v_l)^2]}{[1-4(v_s/v_l)]/2[1- (v_s/v_l)^2]} \]

Young's Modulus of Elasticity:
\[ E = \left[ \frac{p(v_s^2 * ((3v_l)^2 - (4v_s)^2))}{(v_l^2 - v_s^2)} \right] \]
Shear Modulus: \( G = \rho v_s^2 \)

Bulk Modulus: \( K = \rho [v_l^2 - (4/3)v_s^2] \)

where \( \rho \) is the material's density, \( v_l \) is the longitudinal velocity, and \( v_s \) is the transverse velocity.

3.4.2 Physical Properties

The density was determined by using Archimedes principle, described by ASTM method C 373-88.\textsuperscript{21} This method requires the use of a microbalance, a beaker of ethanol and a support basket for the samples. After the dry mass of specimen was determined (D), the specimen was suspended in a beaker of ethanol from a wire basket that was attached to the arm of the balance, and the suspended mass was recorded (S). After the specimen was removed from the basket, the surface of the specimen was blotted dry, and then saturated mass was immediately recorded (M).

The volume of a sample must take into account the volume that the material displaces, the volume of the open pores and the volume of the closed pores present within the sample:

\[ V_{\text{sample}} = V_{\text{dry}} + V_{\text{open pores}} + V_{\text{closed pores}} \]

The suspended mass represents the difference in mass between the suspended sample and the mass of ethanol displaced by the sample. The saturated mass represents the dry mass of the sample and the mass of ethanol in the open pores. In order to determine the volume occupied by both the open and closed pores, the following analysis can be performed:

\[ V_{\text{open pores}} = (M_{\text{saturated}} - M_{\text{dry}})/\rho \text{ ethanol} \]

\[ V_{\text{dry}} + V_{\text{closed pores}} = (M_{\text{dry}} - M_{\text{suspended}})/\rho \text{ ethanol} \]
\[ V_{\text{bulk}} = V_{\text{open pores}} + V_{\text{closed pores}} + V_{\text{dry}} = (M_{\text{saturated}} - M_{\text{suspended}})/\rho \text{ ethanol} \]

The bulk density of the sample can then be determined as follows:

\[ B = M_{\text{dry}}/V_{\text{bulk}} \]

3.5 ADSORPTION OF POLY (PYRIDINE ETHER -CO- ETHER ETHER KETIMINE)

The PEEKt-pyridine copolymer (mentioned in Chapter 2) was adsorbed onto silica in order to increase adhesion between the silica filler and PEEK matrix material used in this study.

3.5.1 Method of Adsorption onto Silica

The surface characteristics are extremely important when adsorbing a polymer to silica. A hydroxylated surface must be present to offer a free radical to the adsorbing polymer. Fumed silica differs from fused silica in that the silanol surface is coated with methyl groups, rather than hydroxyl groups. Since poly (pyridine ether-co- ether ether ketimine) has a free radical on the nitrogen, it is chemically attracted to a hydroxyl group (an -OH containing functional group). In the adsorption of poly (pyridine ether-co- ether ether ketimine) onto the surface of silica, it is vital that the silica has a hydroxylated surface.\(^{14}\)

Poly (pyridine ether -co- ether ether ketimine) must be dissolved in toluene before it can be adsorbed onto the hydroxylated silica. The ratio of polymer in toluene was varied from 1 mg/ml to 10 mg/ml for 0.07 g silica. The polymer solution was added to the silica powder in 20 ml vials, then allowed to shake, on a gyratory shaker, for 72 hours. After 72 hours, the samples were removed from the shaker, the particles were allowed to settle, and then polymer solution was removed from the vial by using a glass pipette.
3.5.2 Adsorption Isotherms

The concentration of polymer in the solution prior to adsorption and after adsorption was determined by ultra-violet spectroscopy. The polymer solutions were diluted at a polymer/toluene solution ratio of 2 ml/10 ml. This dilution was performed three times. It was necessary to dilute the samples in order to keep from saturating the spectrometer at the wavelength of 284 nm.\(^{22}\) The UV wavelength range scanned for these experiments was from 350 nm to 200 nm, this range was found to be adequate because the peak of interest was at 284 nm. These tests were run with a slit width of 1.0 nm, and an absorbance range of 0 - 5.50. The difference in adsorption at wavelength 284 nm was noted. This difference was related to the concentration calibration curve (Concentration = 0.0223*(Adsorbance Value) - 0.0029) and was used to make the adsorption isotherms. Several adsorption isotherms were acquired, and the isotherm ranges were modeled using the Toth equation:

\[
N = N_0 \cdot C \cdot (b + c^m)^{-1/m}
\]

where \(N_0\) is the maximum amount adsorbed, \(C\) is the concentration, and \(b\) and \(m\) are fitted values.

3.5.3 Mathematical Modeling

If the radius of the particle on which the polymer adsorbs is known, and the desired volume fraction of the polymer coating is known, it is possible to determine the coating thickness of adsorbed polymer.
**Figure 19:** An illustration of the thickness of the polymer with respect to the particle.

In Figure 19, $r$ is the radius of the ceramic particle, $t$ is the thickness of the adsorbed polymer coating and $R$ is the total radius of the ceramic and the adsorbed polymer ($R = r + t$). The following derivation relates the volume fraction of the adsorbed polymer to the radius of the particle, and the thickness of the adsorbed polymer.

Total Volume (copolymerr + Ceramic) = $(4/3)\pi R^3$
Volume of Ceramic = $(4/3)\pi r^3$
Volume of Adsorbed Polymer = $(4/3)\pi R^3 - (4/3)\pi r^3$

**Volume Fraction of Adsorbed Polymer =**

$\frac{\text{Volume of Adsorbed Polymer}}{\text{Total Volume (Polymer + Ceramic)}}$

$= V_f = \frac{(R^3 - r^3)}{R^3}$

For a fixed volume of adsorbed polymer,

$t = R - r = [r^3/(1-V_f)]^{0.3} - r$

For a constant thickness of adsorbed polymer,

$V_f = 1 - (r^3/R^3) = 1 - [r^3/(r+t)^3]$
Figures 20 and 21 graphically show the relationship between volume fraction, particle radius and adsorbed polymer thickness. Figure 20 expresses this relationship in a three dimensional plot from Mathematica™. It can easily be seen that the relationship between particle radius and volume fraction has an exponential shape, and the relationship between adsorbed polymer thickness and volume fraction is quite linear. Figure 21 shows a contour plot of adsorbed polymer thickness as a function of particle radius, for given volume fractions. This plot was done in PV-Wave™.23

3.5.4 Fabrication Trials

As mentioned earlier, the purpose of adsorbing the PEEKt-pyridine copolymer onto the silica was to increase adhesion between the silica filler and the PEEK matrix material used in this study. Depending on the initial concentration of copolymer in toluene used, various levels of polymer coverage could be attained. The resulting polymer coated silica had either a monolayer coverage or multi-layer coatings of the PEEKt-pyridine. This coated silica was used to make 1" x 2" x 1/16" composite specimens (40 vol% filler). One sample was prepared attempting to take advantage of the monolayer coverage, another attempted to take advantage of the multi-layer coatings.

For the composite made with the monolayer covered silica, 60 vol % PEEK was used to bind the filler particles together. For the case of multi-layer coatings, no additional PEEK was used - all wetting of the silica that occurred was a result of the adsorbed PEEKt-pyridine copolymer.
Figure 20: Volume Fraction as a function of adsorbed polymer thickness and particle radius.
Figure 21: Volume Fraction as a function of adsorbed polymer thickness and particle radius.
4 Results and Discussion

4.1 Particle Characterization

The PEEK and copper powders were received as bulk powders with a variety of particle size ranges. As discussed in Chapter 3, these powders were separated and analyzed. Table 1 lists the material, particle size range, average particle size, and standard deviation of the particle size for these powders.

The PEEK powder was further characterized. As shown in Figure 4, differential scanning calorimetry (DSC) was performed on the following PEEK particle size ranges: greater than 106 μm, 45+38 μm, and less than 25 μm. From the DSC scan it can be seen that the melt temperature remains unaffected by decreasing particle size. However, the crystallization temperature decreases as particle size decreases. Figure 22 illustrates the relationship between the PEEK particle size and the change in crystallization temperature (Tc) and the change in melt temperature (Tm) of these powders.
<table>
<thead>
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<th>Material</th>
<th>Range (µm)</th>
<th>Average (µm)</th>
<th>Std Dev (µm)</th>
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<td>120</td>
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<tr>
<td></td>
<td>106 + 90</td>
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<td>45 + 38</td>
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<td>10</td>
</tr>
<tr>
<td></td>
<td>38 + 25</td>
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</tr>
<tr>
<td></td>
<td>&lt; 25</td>
<td>22</td>
<td>7</td>
</tr>
<tr>
<td>Copper</td>
<td>&gt; 106</td>
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</tr>
<tr>
<td></td>
<td>106 + 90</td>
<td>96</td>
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<tr>
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Figure 22: The change in melt and crystallization temperatures with particle size.
Figure 23: Crystallization rate versus the material's temperature

a) Crystallization rate vs. temperature for a polymer 24

b) Effect of particle size on effective Tg 9
In order to account for the shift in $T_c$, the observed glass transition temperature of the polymer must decrease as particle size decreases. This makes sense when the polymer's chain mobility is considered as a function of particle size. As the polymer's particle size decreases, its surface area to volume ratio increases; consequently, there are more polymer chains on the surface of the smaller polymer particle than for the larger particle. A chain that is located on the surface of the polymer particle requires less energy to be mobilized to the same extent as when in the bulk (such as in the case of a large polymer particle). The effective glass transition temperature ($T_g$) is the temperature at which a polymer chain becomes mobilized. Therefore, as the polymer's particle size decreases, its effective $T_g$ must decrease also. Figure 23 shows the typical relationship between the rate of crystallization, the glass transition temperature and the melt temperature of the polymer.24

The relationship between the crystallization temperature ($T_c$), melt temperature ($T_m$) and glass transition temperature ($T_g$) depends on thermodynamics and diffusion. Decreasing the glass transition temperature of a polymer would be economically advantageous since less energy would be required to mobilize the polymer's chain to the same extent (i.e., lower processing temperature).

After the PEEK and copper powders were characterized, their particle sizes were matched and mismatched (large PEEK blended with small copper, etc.). These blends were then compression molded. It was found that the smaller particles lead to a more intimately mixed blend. In this study, it was determined that well distributed filler particles are necessary for a 'good' quality, well blended particulate reinforced composite.

For a fixed filler volume fraction, as the filler particle size decreases, the amount of interphase present increases. If the filler were small enough then it would be possible to have essentially all the matrix be in the interphase. As a result, the overall stiffness of the material would be increased because essentially all of the polymer chains will be in contact with the filler surface. This
surface contact partially immobilizes the polymer chains - leading to a greater stiffness.

Several methods were used to gain information on the quality of the composites made. Visual appearance, optical microscopy, C-scan and acoustic microscopy are the methods which were used to determine the initial quality of the samples.

Optical micrographs of the powder blends (found in Appendix A) yielded useful information on the effect of the method of mixing on homogeneity of the powder blends. The examination of powder blend micrographs leads to information about the interaction between the matrix and filler materials.

Some reinforcements did not mix well, and, therefore, produced inhomogeneous composites. The most severe of these were visibly segregated on a macroscopic scale. For example, the PEEK/fumed silica samples appear macroscopically inhomogeneous, regardless of mixing method and particle size; however, the PEEK/copper samples always appear macroscopically homogeneous. The effect of mixing method on the matrix/filler particle interaction can be seen in Figures A5 & A6.

Ultrasonic C-scan and acoustic microscopy were performed to gain information on the homogeneity of the molded composites. Ultrasonic C-scan results, in the form of line-intensified amplitude recordings are shown in Figure 24. The presence of spots (whether light or dark) indicates a change in density of the specimen. The copper filled PEEK (24-a) was tested under the following conditions: a frequency of 2.25 MHz, a 1.125" focal length, a 3.0" element diameter and a gain of 44 dB. This specimen shows a constant intensity of returned signal, characteristic of a homogeneous material. The hand mixed hollow silica was tested under the following conditions: a frequency of 10 MHz, a 0.25" focal length, a 1.5" element diameter and gain of 56 dB. Figure 24-b shows a large variation in signal intensity, indicating that this specimen was not macroscopically homogeneous.
Figure 24-a: Hand mixed PEEK/Copper (matched particles sizes at greater than 106 μm)
Figure 24-b: Hand mixed PEEK (greater than 106 μm)/Hollow Silica (approximately 10 μm)
The effect of the mixing method on the resulting composite can be best seen by comparing hand mixed molded plaques versus mechanically mixed hollow silica molded plaques. The hand mixed hollow silica reinforced PEEK composite resulted in a macroscopically inhomogeneous composite. In Figure 25-a, it can be seen that a variation in sample density exists for the hand mixed specimen. This is reflected in the intensity variation of the acoustic micrograph. Figure 25-b shows a relatively homogeneous distribution of silica in PEEK due to being mechanically mixed. This is reflected by the lack of intensity variation that was seen in Figure 25-a. Figure 25-c is a photograph of PEEK >106/hollow silica molded plaques that were gently hand shaken, rigorously hand shaken and mechanically mixed.

**Figure 25-a:** Hand mixed PEEK/hollow silica, as seen by acoustic microscopy
Figure 25-b: Mechanically mixed PEEK/hollow silica, as seen by acoustic microscopy.
Figure 25-c: Photograph comparison of mixing methods
Sixty-three plaques were produced — each was cut by a water-cooled diamond saw into approximately 12 test strips, for a total of 750 test strips used in this study. These powder blend combinations are summarized in Table 2. This table indicates mixing method, homogeneity, bulk density (g/cc) and percent theoretical density (%). These results indicate that the copper, hydroxylated silica (on the micron scale), and hollow carbon reinforcements yield macroscopically homogeneous composites, regardless of mixing method. The hollow silica results in a homogeneous material only when it is rigorously mechanically mixed for five minutes; if hand mixed an inhomogeneous specimen results. The fumed silica reinforced composite is not a macroscopically homogeneous material, regardless of mixing methods (see Figure 26). In the case of the solid silica that was 250 Angstroms in size, the polymer was unable to wet the filler, and no good consolidation was possible. Since fumed and 250 Angstrom sized silica materials do contain agglomerations, there are many reinforcement particles which are not in contact with the polymer. Therefore, the amount of interfacial surface area is reduced, voids are formed and the quality of the composite is lowered. The most intimately mixed blend was obtained by ball milling copper (greater than 106 μm) and PEEK (greater than 106 μm), as seen in Figure 27-a, 27-b and 27-c. Increased ball milling time resulted in a more intimately mixed powder; however, the level of adhesion between the copper and PEEK was not changed.
Figure 26: Photograph of fumed silica
Table 2: Composite properties summary

<table>
<thead>
<tr>
<th>Material</th>
<th>Mixed</th>
<th>Mechanically Mixed</th>
<th>Homogeneity*</th>
<th>Density (g/cc)</th>
<th>% Theoretical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK &gt;106</td>
<td>X</td>
<td>X</td>
<td></td>
<td>4.51</td>
<td>103.28</td>
</tr>
<tr>
<td>4 hour milled</td>
<td></td>
<td></td>
<td></td>
<td>3.57</td>
<td>81.85</td>
</tr>
<tr>
<td>6 hour milled</td>
<td></td>
<td></td>
<td></td>
<td>3.64</td>
<td>83.43</td>
</tr>
<tr>
<td>8 hour milled</td>
<td></td>
<td></td>
<td></td>
<td>3.69</td>
<td>84.57</td>
</tr>
<tr>
<td>Copper 45+38</td>
<td>X</td>
<td>X</td>
<td></td>
<td>4.49</td>
<td>102.97</td>
</tr>
<tr>
<td>Copper &lt;25</td>
<td>X</td>
<td></td>
<td></td>
<td>3.50</td>
<td>80.15</td>
</tr>
<tr>
<td>Hollow Silica</td>
<td></td>
<td></td>
<td>inhomogeneous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hollow Silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid Silica 95</td>
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<td></td>
<td></td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>Solid Silica 25</td>
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<td></td>
<td></td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>250 A Silica</td>
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<td></td>
<td></td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>Fumed Silica 38</td>
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<td></td>
<td>inhomogeneous</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Fumed Silica 5</td>
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<td></td>
<td>inhomogeneous</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>Hollow Carbon</td>
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<td></td>
<td></td>
<td>1.76</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>PEEK 75+53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper &gt;106</td>
<td>X</td>
<td></td>
<td></td>
<td>3.54</td>
<td>81.17</td>
</tr>
<tr>
<td>Copper 45+38</td>
<td>X</td>
<td></td>
<td></td>
<td>3.59</td>
<td>82.28</td>
</tr>
<tr>
<td>porous 45+38</td>
<td>X</td>
<td></td>
<td></td>
<td>3.17</td>
<td>72.64</td>
</tr>
<tr>
<td>Copper &lt;25</td>
<td>X</td>
<td></td>
<td></td>
<td>3.74</td>
<td>85.61</td>
</tr>
<tr>
<td>porous &lt;25</td>
<td>X</td>
<td></td>
<td></td>
<td>3.06</td>
<td>70.12</td>
</tr>
<tr>
<td>PEEK 45+38</td>
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<td></td>
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<td>Copper &gt;106</td>
<td>X</td>
<td></td>
<td></td>
<td>3.72</td>
<td>85.33</td>
</tr>
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<td></td>
<td>3.60</td>
<td>82.60</td>
</tr>
<tr>
<td>Copper &lt;25</td>
<td>X</td>
<td></td>
<td></td>
<td>3.61</td>
<td>82.76</td>
</tr>
<tr>
<td>porous &lt;25</td>
<td>X</td>
<td></td>
<td></td>
<td>3.08</td>
<td>70.58</td>
</tr>
<tr>
<td>PEEK &lt;25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper &gt;106</td>
<td>X</td>
<td></td>
<td></td>
<td>3.67</td>
<td>84.04</td>
</tr>
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<td>X</td>
<td></td>
<td></td>
<td>3.09</td>
<td>70.81</td>
</tr>
<tr>
<td>Copper 45+38</td>
<td>X</td>
<td></td>
<td></td>
<td>3.67</td>
<td>84.03</td>
</tr>
<tr>
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<td>X</td>
<td></td>
<td></td>
<td>3.28</td>
<td>75.16</td>
</tr>
<tr>
<td>Copper &lt;25</td>
<td>X</td>
<td></td>
<td></td>
<td>2.94</td>
<td>67.34</td>
</tr>
</tbody>
</table>

* Samples are homogeneous unless otherwise noted
Figure 27-a: PEEK/Copper (120 μm) powders after ball milling for 4 hours
Figure 27-b: PEEK/Copper (120 μm) powders after ball milling for 6 hours
Figure 27-c: PEEK (120 μm) and copper (120 μm) powders after ball milling for 8 hours
4.2 Influence of Particle Size on Fabrication

The effect of particle size on processing becomes evident in Table 3. An increase in applied load was required as both the matrix and filler particle sizes decreased. Also, the highest surface porosity was noted for both the smallest filler (less than 25 \( \mu \text{m} \)) and the smallest matrix particle sizes (less than 25 \( \mu \text{m} \)).

Table 3: The effect of particle size on the variables of applied load and surface porosity

<table>
<thead>
<tr>
<th>Copper</th>
<th>&gt;106 ( \mu \text{m} )</th>
<th>75+53 ( \mu \text{m} )</th>
<th>45+38 ( \mu \text{m} )</th>
<th>&lt;25 ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no porosity</td>
<td>no porosity</td>
<td>no porosity</td>
<td>slight porosity</td>
</tr>
<tr>
<td></td>
<td>3000 lb applied</td>
<td>3000 lb applied</td>
<td>5000 lb applied</td>
<td>4500 lb applied</td>
</tr>
<tr>
<td>75+53 ( \mu \text{m} )</td>
<td>slight porosity</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5000 lb applied</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>45+38 ( \mu \text{m} )</td>
<td>no porosity</td>
<td>no porosity</td>
<td>no porosity</td>
<td>porosity</td>
</tr>
<tr>
<td></td>
<td>4000 lb applied</td>
<td>5000 lb applied</td>
<td>4000 lb applied</td>
<td>4250 lb applied</td>
</tr>
<tr>
<td>&lt;25 ( \mu \text{m} )</td>
<td>no porosity</td>
<td>porosity</td>
<td>porosity</td>
<td>porosity</td>
</tr>
<tr>
<td></td>
<td>4500 lb applied</td>
<td>5000 lb applied</td>
<td>4000 lb applied</td>
<td>5000 lb applied</td>
</tr>
</tbody>
</table>
4.3 Mechanical Properties

The primary mechanical properties, such as strength-at-failure, strain-to-failure, and stiffness were determined by three-point-bend flexure tests (described in the previous chapter). Figure 28 shows the range of behavior observed for the various composites that were tested. Graphs showing the flexural behavior of representative composites tested in this study are shown in Appendix B. As expected, the addition of particulate reinforcements improves the stiffness of the polymer. In addition, as the size of the reinforcements decreases, the stiffness increases. In each case, the copper reinforced composite has a higher strength than the silica reinforced composite. This suggests a more effective transfer of load to the reinforcement in the metal composite, and concurs with the idea that the polymer/metal interface is superior to the polymer/silica interface. In addition, the copper powder proved to be more effective in stiffening the polymer than the hydroxylated silica and hollow carbon particles. The stiffening that resulted from the fumed silica was slightly better than the copper; however, the copper was much more homogeneous.

Table 4 summarizes the strength-at-failure, strain-to-failure and stiffness of the specimens under three-point-bend. The values were calculated according to linear beam theory equations. Limitations exist for flexure tests, and these limitations will be addressed in Chapter 5; however, a relative comparison of the variation in Young's modulus with the changes in particle size and composition can still be made.
Figure 28: An illustration of the range of behavior observed for the composites tested in this study.
Table 4: The strength-at-failure, strain-to-failure and stiffness of the specimens under three-point-bend and the respective standard deviations

<table>
<thead>
<tr>
<th>Material</th>
<th>P/Placer ratio</th>
<th>Strength (MPa (STD))</th>
<th>Strain-failure (%) (STD)</th>
<th>Stiffness (GPa (STD))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Cu 4 hr milled</td>
<td>1.0</td>
<td>95.00 (3.56)</td>
<td>2.13 (0.41)</td>
<td>10.44 (0.43)</td>
</tr>
<tr>
<td>P/Cu 6 hr milled</td>
<td>2.8</td>
<td>94.42 (2.25)</td>
<td>2.18 (0.22)</td>
<td>10.31 (0.32)</td>
</tr>
<tr>
<td>P/Cu 8 hr milled</td>
<td>5.5</td>
<td>96.24 (4.49)</td>
<td>1.85 (0.36)</td>
<td>11.21 (0.57)</td>
</tr>
<tr>
<td>P 120/ Cu 120</td>
<td>5.5</td>
<td>97.30 (8.34)</td>
<td>2.26 (0.75)</td>
<td>4.98 (0.91)</td>
</tr>
<tr>
<td>P 120/Cu 43</td>
<td>1.4</td>
<td>103.70 (16.4)</td>
<td>1.59 (0.34)</td>
<td>6.70 (0.95)</td>
</tr>
<tr>
<td>P 120/Cu 22</td>
<td>0.5</td>
<td>89.90 (7.08)</td>
<td>1.21 (0.11)</td>
<td>7.51 (1.16)</td>
</tr>
<tr>
<td>P 120/Cu 22 *</td>
<td>0.5</td>
<td>59.97 (5.67)</td>
<td>1.09 (0.18)</td>
<td>5.56 (0.82)</td>
</tr>
<tr>
<td>P 60/Cu 120</td>
<td>2.7</td>
<td>100.7 (14.3)</td>
<td>1.62 (0.28)</td>
<td>10.08 (2.32)</td>
</tr>
<tr>
<td>P 60/Cu 60</td>
<td>0.3</td>
<td>96.62 (6.16)</td>
<td>1.86 (0.29)</td>
<td>7.68 (0.22)</td>
</tr>
<tr>
<td>P 60/Cu 43</td>
<td>1.4</td>
<td>111.34 (8.26)</td>
<td>2.17 (0.15)</td>
<td>9.24 (1.87)</td>
</tr>
<tr>
<td>P 60/Cu 22</td>
<td>1.0</td>
<td>81.27 (10.8)</td>
<td>1.44 (0.03)</td>
<td>8.51 (1.44)</td>
</tr>
<tr>
<td>P 43/Cu 120</td>
<td>2.7</td>
<td>96.42 (6.16)</td>
<td>1.84 (0.26)</td>
<td>8.04 (0.33)</td>
</tr>
<tr>
<td>P 43/Cu 43</td>
<td>0.5</td>
<td>102.65 (9.88)</td>
<td>1.84 (0.14)</td>
<td>7.88 (1.67)</td>
</tr>
<tr>
<td>P 43/Cu 22</td>
<td>0.5</td>
<td>76.54 (10.9)</td>
<td>1.48 (0.19)</td>
<td>7.88 (2.27)</td>
</tr>
<tr>
<td>P 22/Cu 120</td>
<td>0.2</td>
<td>87.75 (15.8)</td>
<td>2.01 (0.19)</td>
<td>6.88 (1.61)</td>
</tr>
<tr>
<td>P 22/Cu 43</td>
<td>1.0</td>
<td>66.69 (3.1)</td>
<td>1.56 (0.48)</td>
<td>5.54 (1.38)</td>
</tr>
<tr>
<td>P 22/Cu 22</td>
<td>1.2</td>
<td>79.75 (1.16)</td>
<td>1.35 (0.15)</td>
<td>8.23 (1.05)</td>
</tr>
<tr>
<td>P 120/H 10</td>
<td>3.2</td>
<td>80.44 (6.0)</td>
<td>2.29 (0.18)</td>
<td>5.26 (0.59)</td>
</tr>
<tr>
<td>P 120/ S 95</td>
<td>1.3</td>
<td>87.00</td>
<td>5.24</td>
<td>4.55</td>
</tr>
<tr>
<td>P 120/ S 25</td>
<td>4.8</td>
<td>78.58</td>
<td>2.97</td>
<td>3.01</td>
</tr>
<tr>
<td>P 120/ A</td>
<td>4800</td>
<td>8.69</td>
<td>0.84</td>
<td>1.34</td>
</tr>
<tr>
<td>P 120/F &lt;38</td>
<td>2.4</td>
<td>79.13</td>
<td>1.28</td>
<td>10.42</td>
</tr>
<tr>
<td>P 120/F &lt;5</td>
<td>6.0</td>
<td>57.74</td>
<td>0.79</td>
<td>9.45</td>
</tr>
<tr>
<td>P 120/ C 20</td>
<td>1.09 (7.50)</td>
<td>4.28</td>
<td>4.25</td>
<td></td>
</tr>
</tbody>
</table>

P = PEEK, Cu = copper, H = hollow silica, S = solid silica, F = fumed silica, A = 250 Angstrom silica, C = hollow carbon

* porous samples
In addition to the flexural results, Young's modulus was independently determined by means of ultrasonic wave velocity measurements. Using microphone transducers, the specimen was connected to an oscilloscope, and the velocity of the transmitted beam through the material was determined. This velocity is related to Young's modulus through a series of equations as described in Chapter 3. The results are summarized in Table 5. The average modulus values determined by this method are slightly lower than the linear beam theory modulus results. A possible source of error arises because the samples used in this research were thinner than the standard method required (~1.6 mm vs. 5 mm), making it difficult to obtain reproducible echo peaks.

To validate the flexural and acoustic modulus results, tensile tests were performed and Young's modulus was determined for the copper/PEEK samples. The obtained tensile Young's modulus results are summarized in Table 6. The results indicate that the modulus values of the PEEK/copper systems are lower in the tensile tests than in either the flexural or acoustic tests. The elastic modulus of a material remains constant regardless of the test method. Therefore, the obtained tensile modulus values only make sense if one takes into account that these samples had thick tabs with good adhesive bonding. These tabs make it possible for the sample to slip in the grips. This slippage would make the apparent displacement larger; consequently, the calculated elastic modulus would be smaller than expected.

Although the area under the stress-strain curve can be used as a general indication of toughness, a more quantitative measure of impact toughness is desired. The energy adsorbed during impact was measured as described in the previous chapter in order to quantify toughness. The results of these impact tests are given in Table 7.
Table 5: Young's modulus and Poisson's Ratio as determined by ultrasonics

<table>
<thead>
<tr>
<th>Material</th>
<th>P/filler Ratio</th>
<th>Young's Modulus (GPa)</th>
<th>Bulk Modulus (GPa)</th>
<th>Shear Modulus (GPa)</th>
<th>Poisson's Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Cu 4 hr</td>
<td></td>
<td>8.63</td>
<td>10.11</td>
<td>3.18</td>
<td>0.358</td>
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<tr>
<td>P/Cu 6 hr</td>
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<td>7.54</td>
<td>8.00</td>
<td>2.81</td>
<td>0.343</td>
</tr>
<tr>
<td>P/Cu 8 hr</td>
<td></td>
<td>8.73</td>
<td>7.65</td>
<td>3.08</td>
<td>0.323</td>
</tr>
<tr>
<td>P 120/Cu 120</td>
<td>1</td>
<td>8.51</td>
<td>10.66</td>
<td>3.11</td>
<td>0.367</td>
</tr>
<tr>
<td>P 120/Cu 43</td>
<td></td>
<td>7.88</td>
<td>9.97</td>
<td>2.88</td>
<td>0.368</td>
</tr>
<tr>
<td>P 120/Cu 22</td>
<td>5.5</td>
<td>15.38</td>
<td>5.94</td>
<td>7.20</td>
<td>0.089</td>
</tr>
<tr>
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<td>8.19</td>
<td>12.35</td>
<td>2.95</td>
<td>0.389</td>
</tr>
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<td>6.46</td>
<td>8.04</td>
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<td>0.366</td>
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<td>6.61</td>
<td>7.96</td>
<td>2.43</td>
<td>0.361</td>
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<tr>
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<td>6.88</td>
<td>10.20</td>
<td>2.48</td>
<td>0.388</td>
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<tr>
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<td>6.77</td>
<td>7.87</td>
<td>2.50</td>
<td>0.357</td>
</tr>
<tr>
<td>P 43/Cu 43</td>
<td>1</td>
<td>10.18</td>
<td>12.75</td>
<td>3.72</td>
<td>0.367</td>
</tr>
<tr>
<td>P 43/Cu 22</td>
<td>1.9</td>
<td>14.14</td>
<td>5.89</td>
<td>6.43</td>
<td>0.100</td>
</tr>
<tr>
<td>P 22/Cu 120</td>
<td>0.2</td>
<td>6.90</td>
<td>9.64</td>
<td>2.50</td>
<td>0.381</td>
</tr>
<tr>
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<td>6.66</td>
<td>8.89</td>
<td>2.42</td>
<td>0.375</td>
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<tr>
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<td>1</td>
<td>6.70</td>
<td>10.75</td>
<td>2.40</td>
<td>0.396</td>
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</table>

P = PEEK, Cu = copper
<table>
<thead>
<tr>
<th>Material</th>
<th>P/filler ratio</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Cu 4 hr</td>
<td></td>
<td>4.87</td>
</tr>
<tr>
<td>P/Cu 6 hr</td>
<td></td>
<td>5.31</td>
</tr>
<tr>
<td>P/Cu 8 hr</td>
<td></td>
<td>4.98</td>
</tr>
<tr>
<td>P120/Cu 120</td>
<td>1</td>
<td>8.25</td>
</tr>
<tr>
<td>P 120/Cu 43</td>
<td>2.8</td>
<td>7.88</td>
</tr>
<tr>
<td>P 120/Cu 22</td>
<td>5.5</td>
<td>7.66</td>
</tr>
<tr>
<td>P 60/Cu 120</td>
<td>0.5</td>
<td>5.83</td>
</tr>
<tr>
<td>P 60/Cu 60</td>
<td>1</td>
<td>4.25</td>
</tr>
<tr>
<td>P 60/Cu 43</td>
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<td>4.5</td>
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<tr>
<td>P 60/Cu 22</td>
<td>2.7</td>
<td>4.95</td>
</tr>
<tr>
<td>P 43/Cu 120</td>
<td>0.3</td>
<td>4.66</td>
</tr>
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<td>5.86</td>
</tr>
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<td>1.9</td>
<td>3.52</td>
</tr>
<tr>
<td>P 22/Cu 120</td>
<td>0.2</td>
<td>4.34</td>
</tr>
<tr>
<td>P 22/Cu 43</td>
<td>0.5</td>
<td>2.79</td>
</tr>
<tr>
<td>P 22/Cu 22</td>
<td>1</td>
<td>4.2</td>
</tr>
</tbody>
</table>

P = PEEK, Cu = copper
Table 7: Toughness defined as energy adsorbed during impact

<table>
<thead>
<tr>
<th>Material</th>
<th>P/filler ratio</th>
<th>Energy (mJ (STD))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Cu 4 hr</td>
<td></td>
<td>90 (40)</td>
</tr>
<tr>
<td>P/Cu 6 hr</td>
<td></td>
<td>100 (20)</td>
</tr>
<tr>
<td>P/Cu 8 hr</td>
<td></td>
<td>110 (&lt;10)</td>
</tr>
<tr>
<td>P 120/Cu 120</td>
<td>1</td>
<td>130 (30)</td>
</tr>
<tr>
<td>P 120/Cu 43</td>
<td>2.8</td>
<td>140 (40)</td>
</tr>
<tr>
<td>P 120/Cu 43 *</td>
<td>2.8</td>
<td>70 (20)</td>
</tr>
<tr>
<td>P 120/Cu 22</td>
<td>5.5</td>
<td>10 (20)</td>
</tr>
<tr>
<td>P 120/Cu 22 *</td>
<td>5.5</td>
<td>40 (&lt;10)</td>
</tr>
<tr>
<td>P 60/Cu 120</td>
<td>0.5</td>
<td>150 (50)</td>
</tr>
<tr>
<td>P 60/Cu 60</td>
<td>1</td>
<td>90 (20)</td>
</tr>
<tr>
<td>P 60/Cu 43</td>
<td>1.4</td>
<td>150 (30)</td>
</tr>
<tr>
<td>P 60/Cu 43 *</td>
<td>1.4</td>
<td>80 (10)</td>
</tr>
<tr>
<td>P 60/Cu 22</td>
<td>2.7</td>
<td>110 (20)</td>
</tr>
<tr>
<td>P 60/Cu 22 *</td>
<td>2.7</td>
<td>20 (&lt;10)</td>
</tr>
<tr>
<td>P 43/Cu 120</td>
<td>0.3</td>
<td>100 (40)</td>
</tr>
<tr>
<td>P 43/Cu 43</td>
<td>1</td>
<td>170 (10)</td>
</tr>
<tr>
<td>P 43/Cu 22 *</td>
<td>1.9</td>
<td>50 (&lt;10)</td>
</tr>
<tr>
<td>P 22/Cu 120</td>
<td>0.2</td>
<td>90 (40)</td>
</tr>
<tr>
<td>P 22/Cu 43 *</td>
<td>0.5</td>
<td>50 (10)</td>
</tr>
<tr>
<td>P 22/Cu 22 *</td>
<td>1</td>
<td>70 (10)</td>
</tr>
<tr>
<td>P 22/Cu 22 *</td>
<td>1</td>
<td>50 (10)</td>
</tr>
<tr>
<td>P 120/H</td>
<td>12</td>
<td>30 (20)</td>
</tr>
<tr>
<td>hand mixed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 120/H</td>
<td>12</td>
<td>40 (20)</td>
</tr>
<tr>
<td>2 min mech. mix.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 120/H</td>
<td>12</td>
<td>60 (10)</td>
</tr>
<tr>
<td>5 min mech. mix.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 120/S 95</td>
<td>9.5</td>
<td>140 (40)</td>
</tr>
<tr>
<td>P 120/S 25</td>
<td>4.8</td>
<td>160 (20)</td>
</tr>
<tr>
<td>P 120/A</td>
<td>4800</td>
<td>&lt;10 (&lt;10)</td>
</tr>
<tr>
<td>P 120/F &lt;38</td>
<td>3.2</td>
<td>20 (20)</td>
</tr>
<tr>
<td>P 120/F &lt;5</td>
<td>2.4</td>
<td>10 (&lt;10)</td>
</tr>
<tr>
<td>P 120/C</td>
<td>6</td>
<td>50 (30)</td>
</tr>
</tbody>
</table>

P = PEEK, Cu = copper, H = hollow silica, S = solid silica,
F = fumed silica, A = 250 Angstrom silica, C = hollow carbon

* porous samples
Failure mode was studied using SEM and the fracture surface micrographs are in Appendix C. Figures C1, C5 and C7 are representative fracture surface micrographs for the PEEK >106 μm/Copper system. Figure C1 shows PEEK >106 μm/Copper >106 μm. Figures C2-C4 show 8 hour, 6 hour and 4 hour milled PEEK >106 μm/Copper >106 μm, respectively. Figures C5 and C6 show PEEK >106 μm/ Copper 45+38 μm. Figure C7 shows PEEK >106 μm/Copper <25 μm.

The presence of exposed metal particles demonstrates the poor adhesion between the matrix and reinforcement. Figure C6 shows indications that with smaller particle sizes there may be regions of better adhesion. The fracture surface for the composite system of PEEK >106 μm/Copper <25 μm is shown in Figure C7. This figure shows many copper particles that are not in intimate contact with the PEEK. This indicates that a very weak interface exists within this system. This would be expected since the systems with copper <25 μm were the most difficult to process. The difficulty in processing in most clearly seen in the visually observed voids, and increase in time and temperature needed to consolidate the specimens.

Figures C2-C4 show the milled Copper/PEEK systems. These micrographs reveal that the overall distribution of the copper in the PEEK appears more intimate and homogeneous than in the PEEK >106 μm/Copper >106 μm systems. In addition, they reveal that some of the copper particles have been flattened into disks. This changes the aspect ratio of the filler, and could alter the mechanical behavior of the material.

Wetting is required for good adhesion; however, good wetting does not mean that good adhesion has resulted. The effect of particle size on the wetting of the polymer on the filler was observed in this study. An increase in the amount of wetting of PEEK on the copper particles was noticed as the size of the polymer particles decreased from an average of 120 μm to 43 μm (Figures C8 - C10). The greatest level of wetting occurred with the copper
particles which were of matched particle size (Figure C9). Figure C10 is a micrograph of a PEEK 45+38 μm /Copper <25 μm sample. These fillers did not experience the same level of wetting as the PEEK 45+38 μm filled with copper particles in the ranges of greater than 106 μm and 45+38 μm. Figure C10, also, illustrates the size of the voids that were formed during processing in the PEEK 45+38 μm /Copper <25 μm specimens.

As the size of the polymer particles decreased to 22 μm, increased wetting occurred with the copper particles which were greater than 106 μm (Figure C11). This did not appear to be the case with the composites that had fillers of approximately 33 μm and 14 μm in size (see Figures C12 and C13 respectively).

In all of these cases, matrix cracking followed by particulate debonding is clearly the predominant failure mode. Although, with matched matrix and filler particle sizes at 43 μm, an increase in crack deflection through the matrix occurred. This infers that, in general, the crack was deflected around the filler particle at the interface in the PEEK/Copper systems, regardless of matrix and filler particle sizes. Because less energy was required to move the crack around the particle than through it, a weak interface must exist between copper and PEEK.

Figure C14 is a fracture surface micrograph of PEEK/Hollow Carbon, showing residually adhered resin. This would seem to indicate an improved interface. The primary failure mode for this system would be crack deflection, rather than forming the relatively flat fracture surface of Figures C1 - C7.

The fracture surface micrograph of Figure C15 is of PEEK/ hydroxylated solid silica ~95 μm. Figure C16 shows the fracture surface micrograph of PEEK/Hydroxylated solid silica ~9 μm. In both cases, the primary failure mode was debonding. The fracture surface of PEEK reinforced with hollow glass spheres can be seen in Figure C17. In this case, as with the hydroxylated silica, the primary failure mode was debonding; however, some of the hollow silica particles were cracked which indicates that the crack was not
completely deflected by the presence of the filler. The presence of exposed silica particles demonstrates the poor adhesion between the matrix and reinforcement.

Figure C18 shows the fracture surface of PEEK greater than 106 μm filled with 250 Angstrom hydroxylated silica. It is evident from this micrograph that the PEEK was not able to wet the surface of the reinforcement. The presence of exposed silica and matrix particles demonstrates the poor adhesion between the matrix and reinforcement. It appears that the matrix and reinforcement particles are attracted to one another due to static attraction. Consequently, the failure mode for this case was simply matrix and reinforcement debonding due to the presence of a crack.

With fumed silica as the reinforcement, resin rich areas exist within the composite. As seen in Figure C19, the fracture surface is forced to move around the reinforcement particles in a convoluted path, rather than forming the relatively flat fracture surfaces seen with the copper and hydroxylated silica.

Although the micrographs reveal weak adhesion between the copper and the PEEK, the strength and stiffness of the metal reinforced PEEK indicate that load is indeed being transferred to the reinforcement at low strains. These results indicate that the interface is the weakest link in the composite during failure.

The hollow carbon reinforced PEEK shows a slight increase in strength, with little increase in stiffness. These results indicate that the interface is the weakest link in the composite during failure, but that the quality of the interface is good at low strains.

The hydroxylated silica micrographs indicate weak adhesion with the resin. This is supported by the nominal increase in strength and stiffness. These results indicate that the load is not being effectively transferred to the reinforcement, even at low strains.

The fumed silica micrographs indicate that good adhesion does occur for the surfaces of the reinforcement that are in contact with the resin. The reinforcements are not well distributed through out
the composite, so the maximum transfer of load from the matrix to the reinforcement does not occur. Regardless of the homogeneity, there appears to be an increase in stiffness for the fumed silica reinforced PEEK.

4.4 Adsorption Technique

As described in Chapter 3.5, poly (pyridine ether -co- ether ether ketimine) was successfully adsorbed onto the surface of 250 Angstrom hydroxylated silica in order to increase the adhesion between the silica filler and PEEK matrix materials. As seen in Figure 29, an adsorption isotherm was obtained for this system. This isotherm has an initial region of increasing amount of polymer adsorbed, then a plateau region, and then another region of increasing amount of polymer adsorbed. The plateau region is the region of monolayer coverage of the polymer on the silica. The second region of increasing amount adsorbed is the region where a multilayer coverage is formed on the silica. The data was fit to the Toth equation. Three fits of the Toth equation are plotted along with the adsorption isotherm, the respective values for the Toth constants are, also, listed on the figure.
Figure 29: Adsorption isotherm of polymer onto silica
4.5 General Discussion
The quality of a composite can be determined in many ways. The definition of 'good' quality that was used during this study was a well blended composite. Therefore, the effects of particle size changes (either in the matrix or filler) could be more easily studied.

Effect of Particle Size on PEEK
The effect of particle size on the glass transition temperature (Tg) of the PEEK powder was the first noticeable effect of particle size. This becomes important when processing the powder, either as a composite or as a polymer. Decreasing the Tg means that less energy would be required to excite the polymer's chains to the same degree of mobility. As a result, as the particle size of the polymer decreases, it could be processed either at a lower temperature or for a shorter time.

Effect of Particle Size on Processing
The next noticeable effect of particle size focuses on the processability of the composites made in this study. PEEK particle sizes and copper particle sizes are compared in Figure 30 as a function of the ease of processing. The smallest copper particle size range (average particle size of 14 μm) was the most difficult to process, regardless of the polymer particle size. These composites had the most voids -- and the least wetting of PEEK on the copper. The composites that required the least care (but the most processing time) were the largest copper particles -- with an average particle size of 110 μm.
**Figure 30:** Processing summary for PEEK/Copper composites
Effect of Particle Size on PEEK/Copper Composite

The effect of particle size (matrix and filler) on the modulus of the composite is best summarized in Figure 31. As the PEEK particle size is held constant at greater than 106 microns and the copper particle size decreases, the linear beam theory Young's modulus values increase slightly. As the PEEK is held constant at 43 microns and the copper particle size decreases, the linear beam theory Young's modulus values remain constant. As the PEEK is held constant at 25 microns and the copper particle size decreases, the modulus values experience a general increase (poor processing and the presence of voids accounts for the slight decrease at 43 microns).

The most noticeable trend of increasing modulus values occur for the milled samples. The unmilled PEEK 120 μm/Copper 120 μm sample was taken as the 0 hour reference value. Shown in Figure 32, the values are listed in order of increased mill time (0, 4, 6, and 8 hours respectively). These specimens all have modulus values greater than the other PEEK/copper combinations (by more than 2x). The effect of ball milling on the modulus may be attributed to one of the following possible factors: the decreased particle size of the polymer, the increased intimacy of the blend, or the change in aspect ratio of the copper that was noticed.

The modulus values that resulted from the acoustic tests were slightly lower than the flexural results (although the overall results were fairly comparable).

The modulus values that resulted from the tensile tests were low (4 GPa vs. 6 - 8 GPa). These lower modulus values were not unexpected because of two main reasons: the samples were smaller than a standard tensile test specimen, and grip slippage was a problem.
Figure 31: Linear Beam Theory Young's Modulus as a function of Copper particle size
Figure 32: Linear Beam Theory Young's Modulus as a function of Hours Milled
Effect of Particle Size on the Adsorption Technique

The adsorption of the PEEK$_t$-pyridine polymer onto hydroxylated silica was successful, at both low and high coating levels. However, using the polymer adsorbed silica in the processing of a composite was unsuccessful. When these samples were processed, good consolidation did not occur - - the polymer charred and the resulting composite was powdery. Utilizing this adsorption technique in the successful processing of a composite should be the topic of further research.
5. Mathematical Models

Many mathematical models have been proposed to predict the behavior of composite materials. These models take into account the properties of the matrix and reinforcement components and the shape of the reinforcement phase. These models have resulted in equations which can be used to calculate specific properties of the composite. In this chapter, the calculations of a few of these models will be examined as approximations to the experimental data gathered in this study. Simple, general models will be examined as upper and lower bounds, or used as approximations of the measured material properties. This will lead to a general understanding of the experimental results, rather than a quantitative prediction.

5.1 Voigt-Reuss and Hashin-Shtrikman Bounds

The rule-of-mixtures (Voigt upper bound) and the inverse-rule-of-mixtures (Reuss lower bound) provide good first order approximations of composite properties in a wide variety of cases. For this model, the matrix phase is assumed to be continuous, while the reinforcement phase can be either continuous or discontinuous. Consequently, these models will be used to calculate upper and lower bounds for the elastic modulus.
Figure 33: An illustration of Isostrain and Isostress
The Voigt bound is an upper bound, which describes the material which has a load that is applied under isostrain conditions, see Figure 33. This means that the matrix and reinforcement experience the same level of strain. Since the matrix and reinforcement typically have different moduli, they will experience different levels of stress that can be summed to give the total stress level. These conditions may be written as:

\[ \varepsilon_c = \varepsilon_m = \varepsilon_r \]

\[ \sigma_c / \varepsilon_c = V_m \sigma_m / \varepsilon_c + V_r \sigma_r / \varepsilon_c \]

where \( \varepsilon \) is strain, \( \sigma_c \) is stress, and the subscripts indicate "composite", "matrix" and "reinforcement", respectively. These subscripts will be used throughout the rest of this chapter. Substituting the linear, elastic expression \( \sigma = \varepsilon E \) into the sum of stresses equation above yields the traditional rule-of-mixtures expression for Young's modulus:

\[ E_c = V_m E_m + V_r E_r \]

where \( E \) is elastic modulus and \( V \) is volume fraction.

The Reuss bound is a lower bound. If described by the Reuss bound, the load is applied to a specimen under isostress conditions, see Figure 33. This means that the matrix and reinforcement experiences the same level of stress. The matrix and reinforcement undergo different amounts of strain that can be summed to give the total strain level. These conditions are written as:

\[ \sigma_c = \sigma_m = \sigma_r \]

\[ (\varepsilon_c / \sigma_c) = V_m (\varepsilon_m / \sigma_c) + V_r (\varepsilon_r / \sigma_c) \]

Substituting the linear elastic expression \( \varepsilon = \sigma / E \) into the sum of strains equation above yields the following expression for Young's modulus:
\[ \frac{1}{E_c} = \frac{V_m}{E_m} + \frac{V_r}{E_r} \]

The Hashin-Shtrikman Expressions are applicable when one phase, the matrix, is continuous, and one phase, the reinforcement, is discontinuous. The upper bound of the Hashin-Shtrikman Expressions assumes that the continuous phase (the matrix) is the 'hard' phase, and the discontinuous phase (the reinforcement) is the 'soft' phase. The expression for this upper bound on the bulk modulus can be written as follows:

\[ K_U = K_r + V_m \left[ \frac{1}{(K_m - K_r)} + \left[ \frac{3V_r}{(3K_r + 4G_r)} \right] \right]^{-1} \]

Where \( V \) is the volume fraction, \( K \) is the bulk modulus \( (E/3(1-2v)) \) and \( v \) is Poisson's ratio, and \( G \) is the shear modulus \( (E/2(1+ v)) \). Young's modulus is directly related to the bulk and shear moduli by:

\[ E = 4KG/(3K + G) \]

The lower bound on the Hashin-Shtrikman Expressions assumes that the continuous phase is 'soft', and the discontinuous phase is 'hard'. This is the case for the composites made in this study. This lower bound expression for the bulk modulus can be written as:

\[ K_L = K_m + V_r \left[ \frac{1}{(K_r - K_m)} + \left[ \frac{3V_m}{(3K_m + 4G_m)} \right] \right]^{-1} \quad (26) \]

Hashin and Shtrikman describe Young's modulus for a composite material by the following relationship:

\[ E_c = E_m * \frac{[E_mV_m + E_r(V_r+1)]/[E_rV_m + E_m(V_r+1)]}{[E_rV_m + E_m(V_r+1)]} \quad (27) \]

Using the basic relationship between Young's modulus and bulk modulus, Poisson's ratio can be estimated by \( v = \frac{[3-(E/K)]}{6} \).

Figure 34 illustrates the relationship between the Voigt-Reuss bounds and Hashin-Shtrikman Expressions.
Figure 34: Comparison of Voigt-Reuss and Hashin-Shtrikman bounds $^{26}$
5.2 Predictive Equations for Strain-to-Failure, Yield Strength, and Toughness

Provided the matrix and reinforcement have different moduli, the strain-to-failure of a composite must be different from its component materials. If the reinforcement is much stiffer than the matrix, the elongation of the reinforcement phase can be neglected, and the strain-to-failure of the composite should be much less than that of the unreinforced resin. In order for the composite to undergo a certain level of strain, the polymer matrix must elongate to a higher local strain to compensate for the reinforcement particles, which essentially contribute nothing to the elongation. Therefore, the polymer may reach its local failure strain level, while the composite experiences a relatively low overall strain.

In the case of no adhesion, the resulting strain-to-failure is much closer to that of the unreinforced polymer. Therefore, large deviations from these predictions may indicate a lack of good matrix/reinforcement bonding.

If the stress/strain curve of the composite is linear (i.e., a linear, elastic material with brittle fracture), as was observed in some specimens in this study, the prediction of strength and toughness becomes simple. If the strain-to-failure and composite modulus is known, then the failure strength can be calculated from the simple linear elastic relationship:

\[ \sigma_f = E \cdot \varepsilon_f \]

Toughness may be estimated by either the area under the stress-strain curve, or by the impact energy adsorbed. In the case of a linear elastic material with brittle fracture, toughness is simply the triangular area:

\[ \text{Toughness} = (1/2) \cdot \varepsilon_f \cdot \sigma_f = (1/2)E \cdot \varepsilon_f^2 \]
Unnotched Charpy impact tests were performed in order to determine the toughness of the specimens. The energy values were calculated by the software used to run these tests. Consequently, the simple relationship described above was not used in this study.

5.3 Relationship between Tensile and Flexural Properties

Different loading conditions exist within a specimen when the specimen is loaded in tension rather than flexure. This leads to different values of fracture strength. This discrepancy can be understood by examining the two different loading conditions. Regardless of the magnitude of the fracture strength values, the effect of particle size on the modulus of the material should remain the same (i.e., as the particle size decreases, the modulus should increase with modest effects on the strength of the material).

When a specimen is loaded in flexure (three-point-bend), the material sees tensile, compressive and shear stresses. The point on the lower surface of the bar directly under the nose of the test fixture is the point of maximum tensile stress. The point of maximum compressive stress is on the upper surface of the bar, directly under the nose of the test fixture. The "span" is the distance between the outer supports of the test fixture. The "depth" is the thickness of the sample in the direction of the applied load. A "span-to-depth ratio" of 16:1 is commonly accepted as sufficient to ensure that the sample fails due to the tensile stresses. The samples used in this study were made to be approximately 1/16" thick so that a span-to-depth ratio of 16:1 would exist at a span of 1 inch. Consequently, the samples used in the flexure tests were expected to fail due to the tensile stresses present during the experiment.

Since flaws act as stress concentrators and failure in brittle materials tends to initiate at the largest flaw in the region under high tensile stress, the failure of a material tested in tension behaves differently than when in flexure. In a tensile test, the
entire specimen experiences the same amount of stress, and the largest flaw in the sample will initiate failure. In a flexural test, only the small region of the sample under the nose of the test fixture is under stress. Consequently, the largest flaw in this small region will initiate failure and it is rare that the largest flaw of the sample lies in this region. This means that the specimens tested in flexure should, statistically, fail at higher stresses. In order to compare how the testing method affects the failure strength, the PEEK/copper composites were examined under both flexure and tensile conditions.

5.4 Comparison of Measured Data to Predictive Models

The Voigt-Reuss and Hashin-Shtrikman bounds model the upper and lower limits for the experimental data. These models are simple approximations to the real behavior of the materials. The modulus and Poisson's ratio properties used in the calculations are listed in Table 8, along with referenced sources. The resulting lower limit predictions for Young's modulus are listed in Table 9 and compared to measured values. Bulk modulus and Poisson's ratio predictions are listed in Table 9 and compared to measured values.

In order to gain a better understanding of how the measured data compare with the models, the elastic modulus data range for the PEEK/Copper system is plotted with the Voigt-Reuss model. This comparison is shown in Figure 35 (the sample region is represented by the vertical line at 40 vol % filler). The specimens examined in this study exhibit isostress behavior. Particulate reinforcements are not required to strain to the same degree as the matrix. Consequently, a largely isostress condition exists within the specimens of this study. In addition, the stiffness of copper is more than twenty times that of PEEK, which means that the contribution of copper to the elongation of the composite will be essentially negligible.
<table>
<thead>
<tr>
<th>Material</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK $^a$</td>
<td>4.1</td>
<td>.4</td>
</tr>
<tr>
<td>Copper $^b$</td>
<td>117.4</td>
<td>.33</td>
</tr>
<tr>
<td>Silica $^c$</td>
<td>72.4</td>
<td>-</td>
</tr>
</tbody>
</table>

$a$ - Reference 28  
$b$ - Reference 29  
$c$ - Reference 14
**Table 9:** Comparison of Range of Measured Moduli and Poisson's Ratio Values to Predicted Values (all units in GPa)

<table>
<thead>
<tr>
<th>Property</th>
<th>Predicted Value</th>
<th>Measured Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>6.67</td>
<td>4.98 - 11.21</td>
<td>Voigt-Reuss</td>
</tr>
<tr>
<td></td>
<td>8.97</td>
<td>6.61 - 10.18</td>
<td>Hashin-Shtrikman</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.79 - 8.25</td>
<td>Flexural Test</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>11.87</td>
<td>7.65 - 12.35</td>
<td>Acoustic Test</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.374</td>
<td>0.323 - 0.396</td>
<td>Hashin-Shtrikman</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Acoustic Test</td>
</tr>
</tbody>
</table>

* Table 9 shows the range of results for all PEEK/Copper particle size ranges studied.*
Figure 35: Modulus data range for all PEEK/Copper specimens in relation to predictive models.
The composite modulus models, discussed in this chapter, are based on the constituent material properties and volume fractions present. These models accurately predict elastic modulus, bulk modulus and Poisson's ratio values of the PEEK/Copper system.

The isostrain/isostress models provide a micromechanics model of the behavior of these composite systems. By using the simple isostress models, experimental results can be explained in terms of the micro-structure of the material.
6. Conclusion

6.1 Summary

The objectives of this thesis were to study the influence of particle size of the matrix and filler constituent materials on not only the processability of, but also the resulting properties of particulate reinforced composite materials fabricated by the dry powder-powder blend process. These objectives have been realized through the following accomplishments:

- The component materials were separated into various particle size ranges and then thoroughly characterized. DSC was used to characterize all phase transitions in PEEK during the molding cycle. Optical microscopy, image analysis software and SEM were used to study the various powder ranges in terms of particle size, shape and interaction.

- Powder mixing methods were varied to determine which method yields the most homogeneous blend of dry powders.

- To increase the adhesion between silica and PEEK, a new method of coating silica with a PEEK co-polymer was developed.
• Matched and mismatched matrix and filler particle sizes were blended using the optimum mixing method. Fabrication of all powders consisted of a process tailored to the use of fine powders. A suitable combination of molding temperature and pressure was determined for each particle size combination studied.

• Sixty-three composite specimens of various matrix/filler particle size combinations were used in this fabrication process. Three particle size ranges of PEEK (120 μm, 43 μm, and 22 μm) were mixed with the same three particle size ranges of copper. In addition, PEEK was used in combination with either hollow silica, solid silica, fumed silica or hollow carbon particles.

• The composites were characterized in terms of mechanical and physical properties. Three-point-bend flexure tests were performed to determine maximum strength, strain-at-maximum strength, and stiffness. Ultrasonic modulus determination and tensile tests were used to verify the flexural stiffness values. Instrumented impact tests were performed to determine toughness. SEM was conducted on the fracture surfaces to determine failure mode.

• Simple isostress and isostrain models were used as upper and lower limits in estimating the behavior of these materials.

These accomplishments lead to the following conclusions:

• The method used to mix the matrix and reinforcement particles was crucial to the homogeneity of the final composite. The blends became homogeneous after mechanically mixing for 5 minutes. Ball milling the blends for 4 - 8 hours offers an intimately mixed blend, with improvement in flexural elastic modulus.
• For a given matrix particle size, as the particle size of the
  reinforcement phase decreases, the flexural elastic modulus
  tends to increase.

• As the matrix particle size decreases, the flexural elastic
  modulus tends to increase.

• Matched matrix and filler particle sizes of 43 μm offers the
  overall "best" composite in terms of the modulus, homogeneity,
  porosity and processability of the composite.

• These composites have been shown to behave in a manner
  comparable to the simple micromechanics model predictions.

• The adsorption of PEEKt-pyridine onto the surface of hydroxylated
  silica works. The conversion of the ketimine to a ketone is
  crucial in allowing for the successful processing of a composite
  which utilizes the adsorbed polymer. The ketimine form of the
  copolymer is needed in order to dissolve the polymer in toluene.
  However, the ketimine form degrades at low temperatures. In
  order to form a high temperature polymer composite, complete
  conversion to a ketone is necessary.

6.2 Applicability of this research

The most obvious application of this research is to the study
of the effect of particle size of both the matrix and filler material
as they become sub-micron and enter the nanocomposite realm.

In current research in the Materials Science and Engineering
Department at Virginia Tech, mechanical alloying (ball milling) of
polymers and polymer based composite systems is being
investigated. Mechanically alloying these powders leads to the
highest level of intimate mixing possible. This highly intimate
mixed state leads to the highest level of homogeneity attainable for the composite powder blend.

The NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites is currently focusing research efforts in the production of various sub-micron sized polymer powders. Ideally, these sub-micron sized polymer powders could be either used as the matrix material in a composite, or mechanically alloyed to produce a unique, blended state of high performance polymers.

6.3 Possible extensions of this research

In continuing this research, a few critical experiments must be performed. Increasing the processability of the composites made from the small matrix and filler particle sizes is crucial to achieving a 'good', void-free composite. Increasing the test strip size is necessary for performing mechanical tests. Finally, the copper surface should be pretreated to minimize the oxide layer, and ensure good adhesion.

The most obvious extension of this research is to the study of the effect of sub-micron sized matrix and filler materials on the mechanical performance of the composite.

Another possible extension of this research centers on the adsorption of PEEKt-pyridine to hydroxylated silica. Adsorption of this polymer onto the hydroxylated silica surface was successful; however, utilizing the polymer adsorbed silica surface in the processing of composites was not as successful. Again, the PEEKt form is necessary in order to adsorb the polymer onto the silica. However, the PEEK form is needed in order to achieve composite properties. Therefore, the next step is to adsorb the PEEKt-pyridine onto the surface of the silica, completely convert the PEEKt-pyridine into PEEK, and compression mold the converted PEEKt-
pyridine/silica into a composite. After this is successfully accomplished, there are two possible paths forward.

The first path forward involves adsorbing a monolayer coverage to the silica's surface. This monolayer coverage would be advantageous when used with PEEK in that the interfacial strength between the silica and PEEK could be increased. This is because the converted PEEK_{t}-pyridine would be intimately linked to the silica surface; yet, it could, also, be intimately joined with the PEEK polymer.

The second path forward involves adsorbing a multilayer coating to the surface of the hydroxylated silica. By adsorbing a multilayer coating, approximately 50 volume %, the necessity of an additional matrix powder might be eliminated.

This work provides an important link between the production of fine powders and the industrial world of composite processing. This research has shown that as the PEEK particle size decreases, the crystallization temperature (and consequently the effective glass transition temperature) decreases. This could be extremely important to industry in that the reduced glass transition temperature could result in either lower processing temperatures or shorter processing times - - an economic incentive to study the behavior of fine and ultra fine polymer powders. Although the composites made in this study were made by a dry powder - powder blend process, it would be intriguing to examine the influence of sub-micron matrix and filler particle sizes on injection molded and extruded parts.
Appendix A:

Optical Micrographs of Various Powder Blends
Figure A1: Optical micrograph of hand mixed PEEK >106 μm/Copper >106 μm powder blend

Figure A2: Optical micrograph of mechanically mixed PEEK >106 μm/Copper >106 μm powder blend
Figure A3: Optical micrograph of hand mixed PEEK >106 μm/Copper 45+38 μm powder blend

Figure A4: Optical micrograph of mechanically mixed PEEK >106 μm/Copper 45+38 μm powder blend
Figure A5: Optical micrograph of hand mixed PEEK >106 µm/Copper <25 µm powder blend

Figure A6: Optical micrograph of mechanically mixed PEEK >106 µm/Copper <25 µm powder blend
Appendix B

Mechanical Properties
Figure B1: Flexural Stress/Strain curves for PEEK > 106 µm with copper reinforcement (reinforcement size used to identify plots)
**Figure B2:** Flexural Stress/Strain curves for ball milled PEEK > 106 μm/Copper >106 μm
Stress vs. Strain for PEEK 43 μm

Figure B3: Flexural Stress/Strain curves for PEEK 45+38 μm
Figure B4: Flexural Stress/Strain curves for PEEK <25 µm
Figure B5: Flexural Stress/Strain curves for PEEK > 106 μm with silica reinforcement
Figure B6: Flexural Stress/Strain curves for PEEK > 106 μm with carbon reinforcement
APPENDIX C:

Fracture Surface Micrographs
Figure C1: Fracture surface of PEEK $>$106 $\mu$m/Copper $>$106 $\mu$m
Figure C2: Fracture surface of PEEK >106 µm/Copper >106 µm
8 hour milled
Figure C3: Fracture surface of PEEK >106 μm/Copper >106 μm
6 hour milled
Figure C4: Fracture surface of PEEK >106 μm/Copper >106 μm
4 hour milled
Figure C5: Fracture surface of PEEK >106 μm/Copper 45+38 μm
Figure C6: Fracture surface of PEEK >106 μm/Copper 45+38 μm
Figure C7: Fracture surface of PEEK >106 µm/Copper <25 µm
Figure C8: Fracture surface of PEEK 45+38 μm/Copper >106 μm
Figure C9: Fracture surface of PEEK 45+38 μm/Copper 45+38 μm
Figure C10: Fracture surface of PEEK 45+38 µm/Copper <25 µm
**Figure C11:** Fracture surface of PEEK <25 μm/Copper >106 μm
Figure C12: Fracture surface of PEEK <25 μm/Copper 45+38 μm
Figure C13: Fracture surface of PEEK <25 μm/Copper <25 μm
Figure C14: Fracture surface of PEEK >106 \( \mu \text{m} \)/
Hollow Carbon Spheres \( \sim 20 \mu \text{m} \)
Figure C15: Fracture surface of PEEK >106 µm/
Hydroxylated Solid Silica ~95 µm
Figure C16: Fracture surface of PEEK >106 μm/
Hydroxylated Solid Silica ~9 μm
Figure C17: Fracture surface of PEEK $>106 \, \mu m$
Hollow silica $\sim 10 \, \mu m$
Figure C18: Fracture surface of PEEK >106 μm/
250 Angstrom Hydroxylated silica
Figure C19: Fracture surface of PEEK >106 μm/
Fumed silica 1-5 μm
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25. Assistance received from Mac McCord, Nondestructive Evaluation Laboratory, Hancock Hall, VA Tech.


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