INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313-761-4700    800-521-0600
Characterization and degradation of polymer composites for orthopaedic applications

Margevicius, Kristen Jockisch, Ph.D.

Case Western Reserve University, 1993
CHARACTERIZATION AND DEGRADATION OF POLYMER COMPOSITES
FOR ORTHOPAEDIC APPLICATIONS

by

KRISTEN JOCKISCH MARGEVICIUS

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

Thesis Advisors:

Stanley A. Brown, D.Eng.
Katharine Merritt, Ph.D.
Abdelsamie Moet, Ph.D.
Thomas W. Bauer, M.D., Ph.D.

Department of Biomedical Engineering
CASE WESTERN RESERVE UNIVERSITY
January 1993
CASE WESTERN RESERVE UNIVERSITY
GRADUATE STUDIES

We hereby approve the thesis of

Kristen Jockisch Margevicius

candidate for the Doctor of Philosophy
degree.*

Signed: [Signature]
(Chairman)

[Signature]

[Signature]

Date 9-1-92

*We also certify that written approval has
been obtained for any proprietary material
contained therein.
CHARACTERIZATION AND DEGRADATION OF POLYMER COMPOSITES FOR ORTHOPAEDIC APPLICATIONS

Abstract

by

KRISTEN JOCKISCH MARGEVICIUS

The purpose of this work was to examine the interaction between the physiological environment and polymer composite materials intended for use in orthopaedic applications. This was accomplished through three primary objectives. The first objective was to evaluate the use of small-scale flexural test specimens for composite material characterization. Miniflexbars were cut from injection-molded CFRPEEK bendbars. Variation in flexural properties of these MFBs were shown to correlate with variations in local microstructure within the intact bendbar. An overall decrease in flexural strength was found for the MFBs when compared with the flexural strength of the intact bendbar. This could be explained by microstructural differences in fiber orientation and distribution.

The second objective of this work was to use the characterized specimens in exposure studies to test polymer composites in simulated in vivo environments. MFBs were used to examine the effects of serum on flexural properties of various composites. Injection-molded CFRPEEK MFBs, continuous fiber reinforced PEEK MFBs, and injection molded CFRPSU MFBs were exposed to 10% serum for 36 weeks at 37°C. It was shown that those composite PEEK MFBs that contained more matrix material and more fiber ends preferentially absorbed more
serum solution. However, this did not alter flexural properties. Flexural strength and modulus of exposed CFRPSU MFBs increased compared to the properties of the unexposed MFBs. This was in part attributed to the discovery of pores within the CFRPSU material.

Lastly, in conjunction with evaluation of composite degradation due to exposure to serum in vitro using MFBs, degradation products recovered from composite wear in vivo and in vitro were also evaluated. First, a digestion protocol using concentrated HNO₃ as the digest agent was developed and validated. Submicron particles to particles hundreds of microns in size were recovered from digested tissue, as well as from in vitro generation experiments. Global comparison of Poly-2 particles retrieved from digestion compared to particles seen in histological sections indicated similarities. Poly-2 particles generated in vitro were also similar to those particles digested from tissue.
For Bob

To love is not to gaze steadfast at one another:
It is to look together in the same direction.

- St. Exupery,
  Terre des Homme
ACKNOWLEDGEMENTS

I am grateful for the education I have received and the opportunities I have encountered during my graduate years. I am particularly indebted to Professor Stanley Brown who has served as my research and educational advisor with an attitude of support and enthusiasm. The lessons I have learned in his laboratory will long be remembered. My growth as a researcher was also enhanced by the advice, assistance and expertise of Professor Katharine Merritt. In addition, my work would not have been complete without the invaluable resources and encouragement of Dr. Thomas Bauer and Professor Abdelsamie Moet. I would also like to acknowledge the helpful assistance of Dr. James McMahon with the particle project. From my fellow students I appreciate the friendships and enthusiasm that permeated our day to day work.

Finally I must pay tribute to my family. I have never had to look farther than my parents for exceptional role models. I hope that I will be able to support my children in their endeavors as well as they have supported me in mine. I have also been doubly blessed, for, along with a degree, the rewards of graduate school have included my husband. This is indeed a fortune. I look forward to our conversations many, many years form now remembering how and when we began.

V
# TABLE OF CONTENTS

Abstract.................................................................................................................. ii

Dedication................................................................................................................. iv

Acknowledgements.................................................................................................... v

Table of Contents...................................................................................................... vi

List of Figures............................................................................................................. ix

List of Tables............................................................................................................. xiii

1. General Introduction............................................................................................. 1

2. Characterization.................................................................................................... 8

   2.1. Introduction..................................................................................................... 8

      2.1.1. Flexural Testing...................................................................................... 8

      2.1.2. Size Effect............................................................................................ 13

      2.1.3. Injection-molded Composites............................................................... 16

      2.1.4. Carbon Fiber Reinforced PEEK............................................................ 20

   2.2. Materials and Methods.................................................................................. 21

      2.2.1. Flexural Testing................................................................................... 21

      2.2.2. Polycarbonate MFBs.......................................................................... 25

      2.2.3. I-M 30% CFRPEEK MFBs................................................................. 26

      2.2.4. Density................................................................................................. 28

      2.2.5. Analysis............................................................................................... 29

      2.2.6. Scanning Electron Microscopy............................................................ 32

      2.2.7. Residual Stresses.................................................................................. 33

      2.2.8. Ultradeck Composites................................................................. 35

   2.3. Results........................................................................................................... 37

      2.3.1. Polycarbonate...................................................................................... 38

      2.3.2. Fiber Orientation.................................................................................. 38

      2.3.3. Density................................................................................................. 44

      2.3.4. Flexural Testing................................................................................... 45

      2.3.5. ANOVA............................................................................................... 54

      2.3.6. Scanning Electron Microscopy............................................................ 58

      2.3.7. Residual Stresses.................................................................................. 63

      2.3.8. Ultradeck Composites................................................................. 65

   2.4. Discussion...................................................................................................... 71

3. Exposure.............................................................................................................. 80

   3.1. Introduction................................................................................................... 80

   3.2. Materials and Methods................................................................................ 89

      3.2.1. Materials............................................................................................. 89

      3.2.2. Weight Change.................................................................................... 93

      3.3.3. Serum Exposure................................................................................ 93

      3.3.4. Modulus Testing-30% CFRPEEK...................................................... 95

      3.3.5. Flexural Testing................................................................................ 101

      3.3.6. Enhanced Degradation................................................................. 103

   3.3. Results......................................................................................................... 105

      3.3.1. 18 weeks - 30% CFRPEEK............................................................ 105

      3.3.2. 36 weeks - 30% CFRPEEK............................................................ 112

      3.3.3. Enhanced Degradation - CFRPEEK............................................ 121

      3.3.4. 36 weeks - Continuous Fiber/PEEK.................. 121
4. Particles
4.1. Introduction
4.2. Materials and Methods
   4.2.1. Tissue Retrieved from Patients with Poly-2 Implants for Particle Extraction and Analysis
   4.2.2. Preparation of Tissue for Freeze Drying
   4.2.3. Freeze Drying
   4.2.4. Development of a Tissue Protocol for Particle Recovery and Analysis
     4.2.4.1. Determination of Appropriate Digest Agent
     4.2.4.2. Determination of Methods for Particle Collection
     4.2.4.3. Determination of Methods for Particle Suspension
   4.2.5. Validation of Digestion Protocol
     4.2.5.1. Exposure of HNO₃ on Metal Shavings
     4.2.5.2. Exposure of HNO₃ on Metal, Polymer and Ceramic Particles
     4.2.5.3. Digestion of Control Tissue With Known Particles
     4.2.5.4. Digestion of Retrieved Tissue
   4.2.6. In Vitro Generation of Particles
   4.2.7. Preparation of Particles for LM and SEM
     4.2.7.1. Without Filters
     4.2.7.2. With Filters
   4.2.8. Light Microscopy
   4.2.9. Scanning Electron Microscopy
   4.2.10. Coulter Multisizer Analysis
   4.2.11. Particles from Digestion vs. Particles in Histological Sections
   4.2.12. In Vitro Particles vs. In Vivo Particles
   4.2.13. Poly-2 Particles vs. PEEK particles
4.3. Results
   4.3.1. Digestion of Tissue for Particles
     4.3.1.1. Comparison of Digest Agents
     4.3.1.2. Particle Collection and Suspension
     4.3.1.3. Digest Protocol
   4.3.2. Validation of Digest Protocol
     4.3.2.1. HNO₃ on Metal Shavings
     4.3.2.2. HNO₃ on Particles
     4.3.2.3. Spiked Control Tissue
     4.3.2.4. Retrieved Tissue
4.3.3. Coulter and SEM Limitations..............181
4.3.4. Histology vs. Digestion..................187
4.3.5. In Vitro vs. In Vivo.....................191
4.3.6. Poly-2 vs. PEEK..........................194
4.4. Discussion..................................195

5. Summary......................................200

Literature Cited..................................202
LIST OF FIGURES

Figure 2.1. Moment and shear diagrams for three-point-bending and four-point-bending specimen geometries.................10

Figure 2.2. Schematic of three-point-bending experimental set-up: a) test supports; b) attachment of extensometer for measuring displacement...........................................22

Figure 2.3. Sectioning of injection-molded 30%CFRPEEK bendbars into Y and Z MFBs..........................................................27

Figure 2.4. Determination of the plastic fraction from a) stress-strain curves and b) load-deformation curves..............31

Figure 2.5. Strain gage method to determine residual stresses in the I-M 30%CFRPEEK bendbar...........................................34

Figure 2.6. Schematic showing how the freeform Ultracek composites were formed, and the directions that samples were cut.................................................................37

Figure 2.7. Schematic of fiber orientation in the I-M 30%CFRPEEK bendbar.................................................................40

Figure 2.8a. Light micrograph of fiber orientation in the upper corner of section A. Fibers are predominantly transverse.................................................................42

Figure 2.8b. Light micrograph of fiber orientation at the edge away from the gate in section B. Although most of the fibers are oriented parallel to the edge, there are some fibers that are transverse.................................42

Figure 2.8c. Light micrograph of fiber orientation in the center of section B. Notice the alternating pattern of transverse and longitudinal fibers...............................................43

Figure 2.8d. Light micrograph of fiber orientation in section C showing the angled alignment of fibers.........................43

Figure 2.9. Trends in ultimate flexural stress with position in the I-M 30%CFRPEEK bendbar.................................52

Figure 2.10a. SEM micrograph illustrating carbon fiber orientation in an edge MFB (CZ1-compression side of the fracture surface).........................................................59

Figure 2.10b. SEM micrograph illustrating a region of carbon fiber orientation in a core MFB (CZ7-tension side of the fracture surface).........................................................59
Figure 2.10c. SEM micrograph illustrating matrix ductility in a core MFB (CZ7-tension side of the fracture surface)..............60

Figure 2.10d. SEM micrograph illustrating the transition from uncoated fibers on the tensile side to coated fibers on the compressive side (BZ1). This was typical for many MFBs...........60

Figure 2.11. SEM montage indicating the appearance of the fracture surface from the tensile to the compressive side (BZ1). Both coated and uncoated fibers are observed........61

Figure 2.12. Stress-strain curves from flexural testing 30%CFRPEEK MFBs indicating two typical types of observed failure a) catastrophic failure and b) non-catastrophic or stepwise failure.................................................62

Figure 2.13. Flexural stress, strain and modulus of Ultrapek freeform composite specimens of various dimensions. Depth x width dimensions are given in millimeters.............69

Figure 3.1. Sectioning of unidirectional APC-2 composite into 1.5 mm thick longitudinal and transverse MFBs..................91

Figure 3.2. Sectioning of 30%CFRPSU into MFBs......................92

Figure 3.3a. Correlation between flexural strength and modulus for the Y CFRPEEK MFBs........................................96

Figure 3.3b. Correlation between flexural strength and modulus for the Z CFRPEEK MFBs........................................97

Figure 3.4. Determination of maximum elastic load. The point where the line tangent to the load-deflection curve deviates from the curve was considered to be the elastic load limit.......98

Figure 3.5a. Elastic load limit versus depth for the Y MFBs.....99

Figure 3.5b. Elastic load limit versus depth for the Z MFBs.....100

Figure 3.6. Preliminary modulus testing for three BY MFBs.....102

Figure 3.7. Enhanced degradation experimental set-up for 30% CFRPEEK MFBs..................................................104

Figure 3.8. Modulus testing of the CFRPEEK MFBs up to 24 hours (Z MFBs) or 2 weeks (Y MFBs).................................106

Figure 3.9. Flexural test results for AY and BZ 30% CFRPEEK MFBs after 0 and 18 weeks exposure to 10% serum..................109
Figure 3.10. Flexural stress, strain and modulus for each individual A Y MFBs after 0 and 18 weeks exposure to 10% serum. The MFBs are plotted by position. ..................110

Figure 3.11. Flexural stress, strain and modulus for each individual B Z MFB after 0 and 18 weeks exposure to 10% serum. The MFBs are plotted by position. The control MFBs had been modulus tested, but not exposed. The original MFBs had not been modulus tested or exposed...........................111

Figure 3.12. Percent weight change of 30%CFRPPEEK MFBs after 36 weeks exposure to 10% serum........................................114

Figure 3.13. Flexural test results of Y MFBs and Y, B&C MFBs after 0 and 36 weeks exposure to 10% serum. .........................116

Figure 3.14. Flexural test results of Z MFBs and Z, A&D MFBs after 0 and 36 weeks exposure to 10% serum..........................117

Figure 3.15. Flexural test results of All MFBs and B&C MFBs (both Y and Z) after 0 and 36 weeks exposure to 10% serum........118

Figure 3.16. Flexural test results of A&D MFBs (both Y and Z) after 0 and 36 weeks exposure to 10% serum.................................119

Figure 3.17. Light micrographs of the microstructure close to the fracture surface of CFRPPEEK MFBs. Pores are visible in both a) the unexposed MFBs and b) the MFBs exposed to 10% serum for 36 weeks.................................................................125

Figure 4.1a. SEM micrograph of as-received Ti particles.......170

Figure 4.1b. SEM micrograph of Ti particles after exposure to concentrated HNO₃ for 48 hours at room temperature........170

Figure 4.2a. SEM micrograph of as-received HDPE particles...171

Figure 4.2b. SEM micrograph of HDPE particles after exposure to concentrated HNO₃ for 48 hours at room temperature........171

Figure 4.3. SEM micrograph of an unknown residue observed after digestion and collection of particles from retrieved tissue (#286-formalin fixed).........................................................177

Figure 4.4. Light micrograph of an unknown residue observed after digestion and collection of particles from retrieved tissue (#359-formalin fixed).........................................................178

Figure 4.5a. SEM micrograph of particles collected from digestion of retrieved tissue (#282-unfixed). The arrows point to three particles identified as Ti using EDXA..............180

xi
Figure 4.5b. SEM micrograph of a large 100 μm particle extracted from digestion of retrieved tissue (#282-unfixed). This particle was not identified as metal, however, Ti was found on its surface..............................................180

Figure 4.6. Light micrograph of particles extracted from digestion of unfixed tissue (#282)..............................182

Figure 4.7. Comparison of size distributions of as-received Al₂O₃ particles (Astromet) with Al₂O₃ particles exposed to HNO₃ for 48 hours. Clumping of the exposed particles caused the distribution to be shifted to the right and to flatten out (a). After thorough sonication, the distributions for both particle types overlapped (b)..............................184

Figure 4.8a. Light micrograph of tissue surrounding a Poly-2 implant (#282). The giant cell contains distinguishable polyethylene and black debris..............................................190

Figure 4.8b. Light micrograph of another giant cell from the same tissue (#282). Because the giant cell contains so much black debris, individual particles can not be distinguished......190

Figure 4.9. a) Light micrograph of particles generated in vitro using Poly-2 plates and Ti screws. b) Light micrograph of particles generated in vitro using CFRPEEK plates and Ti screws..192.

Figure 4.10. SEM micrograph of particles generated in vitro using Poly-2 plates and Ti screws. A background film is observed covering the filter. Also evident are small rods which may be bacteria..............................................193

Figure 4.11. SEM micrograph of the same type of particles in Figure 4.10 that were exposed to concentrated HNO₃ for 24 hours to remove the contamination..............................................193
# LIST OF TABLES

Table 2.1. Flexural properties of polycarbonate determined using two different load cells ........................................24

Table 2.2. Flexural properties of polycarbonate MFBs and standard size polycarbonate bending bars..........................39

Table 2.3. Density of 3 CFRPEEK MFBs..................................................46

Table 2.4. Flexural properties of All MFBs and Y and Z MFBs........46

Table 2.5. Flexural properties of MFB subgroups.................................47

Table 2.6. Flexural properties of A&D MFBs........................................50

Table 2.7. Flexural properties of B&C MFBs........................................50

Table 2.8. Plastic Fraction for Y and Z MFBs.........................................55

Table 2.9. Plastic Fraction for MFB subsets...........................................55

Table 2.10. ANOVA results........................................................................56

Table 2.11. Residual Stress Results..........................................................64

Table 2.12. Flexural Properties of Ultracek composite MFBs.............68

Table 2.13. Flexural Properties of Ultracek composites of various dimensions.........................................................68

Table 3.1. Modulus Testing CFRPEEK MFBs............................................107

Table 3.2. Flexural properties of CFRPEEK MFBs after 18 weeks exposure.................................................................107

Table 3.3. Weight change of CFRPEEK MFBs after 18 weeks exposure........................................................................113

Table 3.4. Weight change of CFRPEEK MFBs after 36 weeks exposure.........................................................................113

Table 3.5. Flexural properties of CFRPEEK B&C MFBs after 36 weeks exposure............................................................115

Table 3.6. Flexural properties of CFRPEEK A&D MFBs after 36 weeks exposure..............................................................115

Table 3.7. Flexural properties of CFRPEEK Y MFBs after 36 weeks exposure.................................................................120
Table 3.8. Flexural properties of CFRPEEK 2 MFBs after 36 weeks exposure.................................120
Table 3.9. Weight change of continuous fiber PEEK after 36 weeks exposure..................................122
Table 3.10. Flexural properties of continuous fiber PEEK after 36 weeks exposure..........................124
Table 3.11. Percent weight change of CFRPSU after 36 weeks exposure.........................................124
Table 3.12. Flexural properties of CFRPSU after 36 weeks exposure............................................124
Table 4.1. Tissue for digestion ..................................................142
Table 4.2. Density of chemicals and materials......................147
Table 4.3. Density of solutions................................................147
Table 4.4. Size of beads and powders used in protocol validation......................................................150
Table 4.5. Comparison of digest agents.................................162
Table 4.6. Color of solutions for metals exposed to acids..........168
Table 4.7. AAS results for metals exposed to HNO₃...............168
Table 4.8. Coulter analysis of Ti, HDPE, and Al₂O₃ particles before and after digestion......................173
Table 4.9. SEM and LM analysis of extracted particles............176
Table 4.10. Coulter vs. SEM ..............................................186
Table 4.11 Biographical response to wear particles .............188
1. General Introduction

In this new age of composite technology, fiber reinforced polymers are replacing many traditional engineering materials in a variety of structural applications. High strength, low weight and the ability to govern mechanical properties are qualities of composites that make them desirable. These properties became important to orthopaedic researchers with the recognition of "disuse osteoporosis" or stress shielding in the early 1970's. It was proven (Uthoff & Dubuc, 1971) that the mechanical mismatch between rigid metals used in orthopaedic implants and flexible bone could cause bone to resorb and become locally osteoporotic. The search for materials with mechanical properties similar to bone led to polymer composites.

The future possibilities for using composite materials in orthopaedic implants appeared enormous. Fracture fixation plates, screws, total joints, almost any structural device that consisted of metal or plastic were considered areas of potential application. The lure of finding a material with ideal mechanical and biological properties resulted in the evaluation of a variety of composite systems including: carbon fiber reinforced polymethylmethacrylate (Woo et al., 1974), carbon fiber reinforced epoxy (Hastings, 1978; Bradley et al., 1980; Tayton et al., 1982; Tayton & Bradley, 1983; Howard et al., 1985); carbon fiber reinforced carbon (Jenkins & Grigson, 1979; Bruckman & Huttinger, 1980; Christel, 1986), carbon fiber reinforced ultra high molecular weight polyethylene (UHMWPE)
(Sclippa & Piekarski, 1973), carbon fiber reinforced nylon and polybutylene terephthalate (Gillett et al., 1985), carbon fiber reinforced polysulfone (McKenna et al., 1980; Prakash, 1989; Wenz et al., 1989), and carbon fiber reinforced polyetheretherketone (Williams et al., 1987; Jockisch et al., 1992). Unfortunately, transforming industrial composites into orthopaedic composites has encountered more difficulty than first expected. The orthopaedic community is still waiting for the putative panacea.

The trouble has occurred because of the very nature of composite materials. A variety of choices for matrix material, fiber reinforcement and processing conditions increases versatility in designing new, tailor-made materials. This is complicated, however, by the constant state of development of composite technology. New and better polymers are being combined with new and better fibers. In the late 1970's, the choice of epoxy/carbon composites for bone plates, which have been used clinically (Tayton and Bradley, 1983; Howard et al., 1985), was in large part determined by the dominance of thermoset composites at the time. These composites are limited by their inability to be contoured once fabricated, low shelf life, insufficient toughness, low strain to failure, and moisture sensitivity (Beland, 1990). Despite this, the early thermoplastic polymers used in composites could not compete with the thermosets for high performance applications. Such polymers included polyethylene and polymethylmethacrylate which have flexible carbon chains that can change conformation easily. Rigidity is obtained by restricting the
movement of the chain by crystallinity as in polyethylene or by the introduction of sidegroups as in polymethylmethacrylate. The major limitations of these thermoplastics are their low elastic modulus, low glass transition temperature, and poor solvent resistance (Beland, 1990). Recently, however, high performance thermoplastic composites, such as polysulfone (PSU) and polyetheretherketone (PEEK), have come to the forefront. By including rigid aromatic rings in the polymer chains, intermolecular forces are increased, improving mechanical properties and solvent resistance (Billmeyer, 1984).

As a consequence of this continuous introduction of new generations of composite materials, many different composites have already been evaluated for orthopaedic applications. Some of them, especially the early thermoplastics such as PMMA, nylon, and PBT, were not developed past initial testing, succumbing to the arrival of the better thermoplastics PSU and PEEK. For others, such as carbon/carbon composites, a great deal of time and experimentation was undertaken to develop a hip stem (Christel et al., 1987). However, high costs of testing and processing combined with less than anticipated performance has halted future development of this implant (Meunier, 1992). There have been a few clinical successes, such as the carbon/epoxy bone plates, although their future is uncertain (Sell et al., 1989). There have also been failures with the clinical application of composites, primarily with a carbon fiber reinforced polyethylene composite (Poly-2) used in acetabular cups and tibial
plateaus. The attraction of Poly-2 as an ideal orthopaedic material propelled it into clinical use before adequate understanding of its wear properties was obtained (McKellop et al., 1981). Although this composite has not been clinically successful, much can be learned from clinical experience.

The failure of Poly-2 can be related to another difficulty in the development of polymer composites in orthopaedics, composite characterization. Although experience has been gained with composite characterization for both industrial and orthopaedic applications, standards for testing composites are not yet fully developed (Agarwal and Broutman, 1980; Huettner and Weiss, 1989; Adams, 1991). This is in part due to the increased complexity in characterizing nonhomogeneous, anisotropic composites as compared to characterization of homogeneous, isotropic materials. Composite mechanical and material properties must be related to composite microstructure. Traditional test methods developed for traditional engineering materials must be modified to meet the demands of composite characterization (Adams, 1990). Likewise, tests for characterization of composites should be chosen with the end-use application in mind (Adams, 1990).

This has implications for the composites that are now receiving the most attention for orthopaedic implants, carbon fiber reinforced PEEK and carbon fiber reinforced PSU. Already, these materials are being improved upon by other high performance thermoplastics in industry (Beland, 1990). Even so, past research experience (Brown et
al.}, 1990; Wenz et al., 1990; Magee et al., 1988) indicates that these composites may be suitable for a variety of orthopaedic applications. In order for them to come into widespread acceptance in orthopaedics these composites must be well characterized for their intended application.

In orthopaedic applications, the interaction between the implant and the physiological environment is critical. The in vivo environment can alter the mechanical properties of the implant material; likewise, the implant or degradation products from the implant may induce an unwanted reaction from the surrounding tissue. A full characterization of a potential composite for orthopaedic applications must address these issues.

The purpose of this work was to examine the interaction between the physiological environment and the polymer composite materials intended for use in orthopaedic applications. This was accomplished through three primary objectives based on the need for modified characterization methods as well as the desire to learn from previous clinical experience with composites.

The first objective was to evaluate the use of small-scale flexural test specimens for composite material characterization. As mentioned, composite characterization is not an easy task since mechanical and material properties of composites are critically dependent on processing conditions. As a consequence of processing, most composites exhibit local variations in microstructure. The ensuing anisotropy and/or heterogeneity results in a distribution of
mechanical properties within the composite. Therefore, choosing representative specimens for testing can be quite difficult. One option is to have test specimens be individually molded. These specimens, however, run the risk of being quite different from the material that is used in a device. Another option is to cut small specimens from a mother piece or from the device itself. If specimens are cut from representative sections, and the microstructure of these specimens is known, much information can be gained about the mechanical properties of a device. A small specimen size is necessary so that local variations in mechanical properties can be detected. Keeping specimens small is also advantageous for statistical analysis, since many specimens can be tested. The potential benefit of the use of small sized fracture toughness specimens (Pilliar et al., 1987) and flexion specimens (Brown and Bargar, 1984) have already been shown in the evaluation of bone cement and dental restorative materials.

The second objective of this work was to use the characterized specimens in environmental exposure studies to evaluate PEEK and PSU composites. An advantage of a small specimen size is that small specimens can be readily used in aging experiments both in vitro and in vivo. Because of the larger surface area to volume ratio of small specimens compared to standard size specimens, the effects of various environments on the small specimens may be detected earlier (Wagner, 1989).

Although small sized flexural test specimens are beneficial for
understanding composite mechanical properties and can be used in controlled degradation testing, another aspect of composite degradation includes the wear properties of the composite, and the role of these products when they are generated in vivo. Therefore, the third objective of this work was to evaluate degradation products resulting from the mechanical wear of a polymer composite that has already been clinically used in orthopaedics. This material was carbon fiber reinforced UHMWPE or Poly-2. The clinical failure of acetabular cups and tibial plateaus made of Poly-2 were a consequence of the poor wear properties of Poly-2. In many situations a great amount of UHMWPE, carbon fiber and composite particles were released into the surrounding joint capsule. Gray and black staining of adjacent tissue associated with a histiocytic and foreign body giant cell reaction was observed (Wright et al., 1988; Groth and Shilling, 1983). Polymeric particles liberated into the tissue surrounding total joint replacements due to wear have been implicated in contributing to, and possibly causing implant failure. This association of wear debris with an injurious biological response was first observed by Charnley, the pioneer of total hip implants in the 1960's. Since then the biological response to particulate material has received a great deal of attention. If composites are going to be successfully used in clinical situations where a possibility exists for the release of wear debris (such as bone plates, and total joints), then composite wear debris must be studied.
2. Characterization

2.1. Introduction: The objective of this work was to evaluate miniflexbars (MFBs), 1 x 5 x 30 mm, as specimens for flexural testing composite materials. The motivation for this was two-fold. First, once a method is validated for small scale specimens, the minibars can be used in several tests, primarily environmental exposure testing and conceivably lead to an accelerated degradation test method. Another possibility is using the MFBs in in vivo testing. The small size would allow for multiple specimens to be implanted in a single animal, generating results that can be directly compared with results from in vitro testing. Also, mechanical data from testing these specimens can be useful for small scale devices that are of the same dimensional order, such as struts on a spinal cage implant (Brantigan, 1991).

2.1.1. Flexural Testing: The basis for the MFB method is the testing of miniaturized specimens, 1 x 5 x 30 mm, in flexion. The MFBs were first developed in order to evaluate the flexural properties of retrieved bone cement (Brown and Bargar, 1984). The flexural properties of potential implant materials are particularly important since the type of loading of many orthopaedic devices, such as bone plates and hip stems, is bending. In addition, comparing mechanical properties of implant materials with that of bone generally requires flexural data, especially bending modulus (Woo et al., 1984; Claes, 1989).
There are other advantages of flexural testing over tensile or compression testing which include the ease of sample preparation and the relatively simple test procedure. For experimental testing the ASTM standard test method for flexural properties of unreinforced and reinforced plastics is D790M. This standard contains both three-point-bending and four-point-bending test methods. In these tests a flat specimen is supported at two ends and is loaded by either a central load (three-point-bending) or by two symmetrically placed loads (four-point-bending) (Figure 2.1a,d). A central load in the three point bending produces a bending moment on the beam that varies linearly from zero at the supports to a maximum value at the center (Figure 2.1b). A uniformly distributed shear stress all along its length is also produced (Figure 2.1c). In contrast, in four-point-bending the two symmetric loads produce bending moments that linearly increase from zero at the supports to a maximum value under the load (Figure 2.1e). The bending moment between loads remains constant. No shear stress is produced between the loads, and the middle portion of the beam is subjected to pure bending (Figure 2.1f). Because of the small size of the MFBs only three-point-bending is practical. Therefore, the potential effects of a shear stress must be considered in relation to specimen dimensions.

Tables indicating standard specimen sizes can be found in ASTM D790M. Many of the dimensions for specimens are based on the need to have a sufficient span:depth ratio in order to minimize the effects of shear stress which can obscure the correct value for flexural
Figure 2.1. Moment and shear diagrams for three-point-bending and four-point-bending specimen geometries.
strength. Maximum flexural strength is the theoretical value of stress on the tensile surface of the specimen at failure. In three-point bending it is calculated from the maximum bending moment by assuming a linear stress strain relation to failure. It is given by the expression

$$\sigma = \frac{6M}{bh^2}$$

M = bending moment
h = specimen depth
b = specimen width

where

$$M = \frac{Pl}{4}$$

l = span
P = failure load (at maximum tensile force)

Maximum shear stress in a rectangular beam occurs at the neutral axis (which is the line that separates the part of the beam in tension from the part of the beam in compression). The expression for maximum shear stress is

$$\tau = \frac{3V}{2bh}$$

V = maximum shear force

In three point bending there is competition between the tendency for the beam to fail by tension in the outer fibers of the beam and the tendency of the beam to fail from shear. From the above equations it can be seen that by increasing the span the shear stress is not affected, however the bending moment is increased which increases the tendency for failure by tension. Typically a minimum span to depth ratio of 16:1 is recommended. For this reason, in three-point-bending tests of the MFBs, a 16:1 span:depth ratio is used.
In addition to span and depth, specimen width is also a factor in the above equations. A typical standard specimen size is 6 x 12 x 120 mm (Dexter). For a 16:1 span:depth ratio, the ratio of tensile stress to shear stress ($\sigma/\tau$) for this specimen size is approximately 17. In comparison, the ratio is approximately 11.5:1 for the MFB specimen. Whether or not this will be great enough to assure that failure will occur by tension rather than by shear depends on the material.

For highly orthotropic composites, where the interlaminar shear strength is low compared to the tensile strength, the value calculated for flexural strength may be effected by shear (Agarwal and Broutman, 1980). Failure by interlaminar shear was demonstrated for variable thickness unidirectional composite beams of carbon/PEEK and carbon/epoxy for a minimum span:depth ratio of 12:1 (Miravete and Kim, 1990). Failure occurred in the midplane of the beams where the shear stress was maximum. For these materials a comparative flexural strength is calculated rather than a fundamental flexural strength. Shear deformation can also significantly influence modulus data of highly orthotropic composites. A span:depth of 60:1 is suggested by ASTM. The flexural modulus of laminated composites is also a strong function of ply stacking sequence.

For chopped fiber composites, problems associated with shear are much less when compared to the continuous fiber composites. Generally these composites have tensile to shear, strength and modulus ratios that are greater than 8:1, which is what is
recommended by ASTM for the calculated flexural strength and modulus to be valid (D790M).

2.1.2. **Size Effect:** Another concern is whether or not the strength associated with the 1 mm thick composite MFBs will be different than that of large specimens of the same material simply because of size. A "size effect" has been observed for many materials (Harter, 1977). This effect, although not predicted by D790M, has been described by linear elastic fracture mechanics, and by statistical theories based on critical flaw distribution.

A size effect predicted by fracture mechanics is due to the differences in stress states that occur because of specimen thickness. The stress state in a material can change if specimen thickness is decreased to the point where the state of stress is altered from plane strain to plane stress. In a state of plane strain, the specimen is thick enough so that the sample is constrained by the surrounding material to strain in a plane. For a specimen of smaller thickness the amount of material may not be sufficient to constrain strain to a plane. Therefore, the decreased thickness will not support the load any more in that dimension. This results in a condition of plane stress. These conditions are important since under plane stress the size of the plastic zone will increase three-fold from that of a similar specimen in plane strain (Broek, 1986). Therefore, in plane strain, the amount of plastic deformation (yielding) is less than that would occur in plane stress.
This implies that below a certain thickness threshold, experimentally determined strengths will be greater than for the same material with a greater thickness. Therefore, if the effect exists for composite MFBs, then comparing data from flexural testing MFBs with data from testing standard size bendbars may not be valid.

The size effect phenomena was clearly shown for steels (Green and Knott, 1973). However steels and other monolithic materials do not contain fibers which can also act as constraints. For instance, in an APC-2 (carbon/PEEK) unidirectional laminate, the fibers constrained the matrix from developing a fully yielded region (Crick et al., 1987). Therefore, a thin specimen may still be in plane strain because of the fiber constraints. This is especially true for continuous fiber laminates.

Using fracture mechanics to predict the size effect in laminated composites has been difficult. Problems with applying present day fracture toughness tests to composite laminates primarily resulted from invalid crackgrowth (Herakovich, 1990; Crick et al., 1987). Despite this, in the study of the fracture of APC-2 (carbon/PEEK) of unidirectional laminates approximately 5 mm thick, the size of the damage zone was 0.1 mm (Crick et al., 1987). This is significantly smaller than the 1 mm thickness of MFBs.

However, in another fracture toughness study using graphite/epoxy laminates (Harris and Morris, 1986), laminate thickness significantly influenced notch strength. The strength of the [0/90] and [0/±45/90] laminates decreased with increasing
thickness while the strength of the [0/±45] laminate increased with increasing thickness. The fracture surfaces of the thin laminates were generally nonuniform and the fracture surfaces of the thick laminates were relatively uniform. The authors stated that fracture toughness behaves much like a material property for thicker laminates. This conclusion was reached because fracture toughness of the thicker laminates was shown to be relatively independent of notch size and laminate stacking sequence. For the laminated graphite/epoxy composite, the transition from thin behavior to thick behavior occurred between 3.5 mm and 7.5 mm.

Another method of evaluating a possible size effect is by considering statistical analysis of the critical flaw distribution in a material. As the dimensions of a specimen increase, the volume of the specimen also increases. This results in a cross sectional area that may contain an increased number of defects which can initiate failure. Therefore, especially for brittle materials such as fibers, smaller sized test specimens will exhibit greater strengths than their larger sized counterparts. Although this theory works well for the fibers used in composites (Wagner, 1989), it has not been used to accurately predict size effects in composites, either chopped fiber (Nimmer and Trantina, 1985) or continuous fiber reinforced (Wisnom, 1991).

Whether or not the 1 mm thickness of the MFBs is below a thickness threshold that will be influenced by a size effect cannot be generically determined. Each material must be evaluated
independently. If a size effect is determined, then caution must be taken in comparing flexural results of MFBs with other size specimens. However, comparison between MFBs of different materials is still valid.

2.1.3. **Injection-molded Composites:** Injection-molded 30% chopped carbon fiber reinforced PEEK (CFRPEEK) was chosen as the composite system for evaluation of the use of MFBs for composite characterization. Although local variation in mechanical properties are observed with some continuous fiber composites as a consequence of generated internal stresses and morphological changes (Lawrence et al., 1990), heterogeneity is more readily apparent with chopped fiber composites, particularly those that are injection-molded. Anisotropy in material properties of injection-molded, short-fiber-reinforced thermoplastics is primarily related to flow-induced fiber orientation. The preeminence of fiber orientation in determining mechanical properties has been upheld by recent studies that have predicted mechanical properties with computer modeling based solely on fiber orientation (Ranganathan and Advani, 1990; Matsuoka et al., 1990). Since fiber orientation plays such a key role in the mechanical properties of an injection-molded composite and fiber orientation is easy to evaluate with microscopy, this investigation concentrated on evaluating injection-molded composites.

Injection molding of chopped fiber composites is an efficient processing method that can reduce manufacturing costs and can
facilitate mass production. The mechanical properties of injection-molded materials are dependent on fiber length, fiber volume fraction, fiber orientation and fiber matrix interface strength. These features are affected by processing conditions such as mold geometry, molding temperature, and rheological properties of the molding compound (Wu and Schultz, 1990). Actual fiber length depends on the processing history of the material. Most fiber breakage and abrasion happens when the fibers are not yet fully wetted by the polymer melt in the screw extruder (Shirrell, 1985). The shorter fibers result from larger shear stresses during processing (Wu and Schulz, 1990). The importance of fiber length is due to the critical length of a fiber which is the length that is sufficient to allow the stress transferred through shear at the interface to load the fiber to failure. Although this may seem simple, stresses applied to the fiber are complicated greatly by cracking at the fiber ends, partial debonding and contact with adjacent fibers (Mandell et al., 1982). Fiber clumping also occurs in injection-molded composites. The length of these local agglomerations is similar to the length of the longest fibers in the region, and the fibers end up parallel in orientation. (Mandell et al., 1982)

A consequence of injection-molded parts is a mechanical anisotropy primarily due to flow-induced fiber orientation. Orientation of the fibers is largely determined by the velocity profile of the flow of the plastic (Sherman, 1985). The profile of fiber orientation of highly reinforced thermoplastics (30% fiber
volume or greater) that have been injection-molded has been characterized as having three distinct layers. The outer layer on each side of the part is the "skin" region. In this region, the fibers are predominantly aligned parallel to the direction of flow. The middle or "core" region contains fibers that are aligned perpendicular to the flow direction. This results from near constant velocity in this region. The thickness of the layers is variable and depends on the thickness of the part, fiber volume and processing conditions (Sherman, 1985).

Evaluation of 30% chopped carbon fiber reinforced PEEK injection molded pin edge gated discs revealed anisotropic fracture properties when measured in different directions relative to the mold fill direction (Friedrich et al., 1986). Three main layers of fiber orientation were also detected in the discs. In the two surface layers, the fibers were oriented parallel to the mold fill direction, fibers in the central layer had the opposite orientation. Other work has described injection-molded parts without pronounced skin and core regions, although preferred fiber orientation in the direction of the flow was evident through the thickness of the part (Nimmer and Trantina, 1985).

To determine the variability caused by fiber orientation variations, the relationship between moduli and strength has been used (Shirrell, 1985). From composite micromechanical theory, it is possible to predict that fibers which are oriented parallel to the edge in the load application section of three- or four-point flexure
specimens will substantially increase both the specimen’s strength and modulus. Those fibers which are oriented transverse to the edge of the specimen in the load application section will decrease both the strength and modulus. Thus, the presence of any locally oriented fibers should result in a positive correlation between strength and modulus in flexure specimens. However, there should be no relationship between the strength and modulus of tension specimens since the load in this type of specimen is distributed across a much larger testing section. The nature and number of the flaw sites will determine the strength of the specimens, whereas the homogeneity of the fiber orientation and the fiber distribution across the testing section will determine the specimen’s modulus. Results of flexural tests of injection-molded composites may be unrealistically high due to the fiber orientation at the surface (Nimmer and Trantina, 1985).

Another consequence of injection molding is the introduction of residual stresses in parts. Residual stresses are usually large and compressive near specimen surfaces and small and tensile in the interior. In a flexure test, the ultimate strength is calculated from the outer fiber stress at failure. If failure is assumed to be due to tensile stresses, then the compressive residual stresses at the surface would lead to erroneously high failure predictions (Nimmer and Trantina, 1985). Release of residual stresses can also occur by cutting an injection-molded part. Since MFBs are to be cut from injection-molded bendbars, the effect of residual stresses must be considered when evaluating the flexural test results.
2.1.4. Carbon Fiber Reinforced PEEK: The selection of CFRPEEK was based on its potential for a variety of medical applications. PEEK is one of the few matrix materials being considered for use in orthopaedic implants. A good short-term biological response to CFRPEEK has been demonstrated both in vitro (Wenz et al., 1990) and in vivo (Jockisch et al., 1992). Results from short-term environmental testing of continuous fiber reinforced PEEK in saline solution at 37°C (Hastings, 1987) and at elevated temperatures (Maharaj et al., 1991) are also promising. Additionally, the influence of microstructure on various properties of injection-molded CFRPEEK have been shown. Specifically, differences in thermoelastic properties were found in injection-molded dogbone tensile specimens containing three distinct layers of fiber orientation (Bozarz et al., 1987). This layering was also observed in injection-molded pin edge gated discs, with resulting anisotropic fracture properties (Friedrich et al., 1986).
2.2 Materials and Methods

2.2.1. Flexural Testing: Miniflexbars (MFBS) were tested in three-point-bending. Other than the choice of specimen size (1 x 5 x 30 mm), ASTM standard D790M-84 was followed. A testing jig was used that had a constant support span of 16.07 mm (Figure 2.2a). Radius of curvature of the loading nose and supports was 0.2 mm. The MFBS were tested at a strain rate of .01 min\(^{-1}\) (0.5 mm/min crosshead rate) with a screw driven mechanical test machine (Scott-CRE/1000).

Connected to the Scott was an X-Y recorder, a strip chart recorder, and a digital multimeter (DMM-Kiehly). The strip chart recorded load versus time. The X-Y recorder plotted load vs deflection, which was determined directly from the Scott crosshead rate. The DMM was connected to the variable potentiometer of the timing device which fine tuned the crosshead rate. A very good linear correlation was found between crosshead rate and DMM output for crosshead rates between 0.26 to 3.12 mm/min. The rate at which the Scott needed to be run for testing the MFBS, however, was at the lower level (.5 mm/min). It was seen that at these slow speeds, the crosshead rate varied, even when the output from the DMM was constant. The variance in the rate was small enough that the outcome of the test would not be affected, but large enough that deflection measured using crosshead rate would be affected. Therefore, the crosshead rate was calibrated for each sample simply by ticking the maximum load switch on the Scott which marked both the XY chart recorder (load vs. deflection) and the stripchart recorder (load vs.
Figure 2.2. Schematic of three-point-bending experimental set-up: a) test supports; b) attachment of extensometer for measuring displacement.
time) at the beginning of the test. At the end of the test, the maximum load switch was ticked again. The distance between the calibration marks when multiplied by the stripchart speed and divided by the distance on the stripchart then gave a better estimate of the crosshead rate.

Deflection was measured in this manner for the freeform samples (see section 2.2.7.). Subsequently an extensometer (MTS model 632 - 118 - 20) was used to measure deflection for all of the other samples except when noted. The extensometer was attached to the moving loading nose and the stationary supports as shown in Figure 2.2b. To determine if any differences existed between strain calculated using crosshead rate and strain calculated using the extensometer, polycarbonate MFBs were tested under the same conditions with and without the extensometer. Results are shown in Table 2.1. Although a significant difference was not calculated between the stripchart (SC) strain vs. the extensometer (EXT) strain, the extensometer strain was decreased approximately 10% compared to the stripchart strain. The variability in strain calculated with the extensometer was also less. Therefore, throughout the tests, strain data was only compared if it was determined by the same method.

Depending on the material (i.e. unreinforced polymer, chopped fiber composite, or continuous fiber composite) and the size (i.e. MFB vs. standard size), either a 245 newton load cell or a 4900 newton load cell was used to measure load. To assure that any differences in mechanical properties that may be observed between
Table 2.1. Flexural stress, strain and modulus for polycarbonate MFBs tested using the large load cell (4900N), the small load cell (245N), the stripchart recorder (SC) and the extensometer (EXT).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4900N-SC</td>
<td>5</td>
<td>104.5 (1.5)</td>
<td>6.21 (.57)</td>
<td>2.81 (.16)</td>
</tr>
<tr>
<td>4900N-EXT</td>
<td>5</td>
<td>107.9 (1.5)</td>
<td>5.44 (.36)</td>
<td>3.07 (.05)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>245N-SC</td>
<td>5</td>
<td>104.8 (1.8)</td>
<td>6.19 (.58)</td>
<td>2.87 (.16)</td>
</tr>
<tr>
<td>245N-EXT</td>
<td>5</td>
<td>105.1 (2.1)</td>
<td>5.59 (.47)</td>
<td>3.00 (.04)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NF</td>
<td>NS</td>
</tr>
</tbody>
</table>
standard size specimens and the MFBs are related to the material/dimensions and are not artifacts caused by changing load cells, mini flexbars cut from acrylic sheet were tested using both the 245 N load cell and the 4900 N load cell. As shown in Table 2.1, no significant differences were seen between stress, strain or modulus for the MFBs tested with the different load cells.

CFRPPEK MFBs (described in section 2.2.3) were tested to failure using the 245 N load cell and the MTS extensometer. Stripchart recordings of load versus time were also taken. Maximum flexural stress, axial strain at maximum stress and flexural modulus were calculated from the curves. Strain was analyzed at maximum stress for consistency, since the load deflection traces after the point of maximum stress was reached varied between specimens.

2.2.2. Polycarbonate MFBs: Since the MFBs were being used to determine local differences in mechanical properties for heterogeneous and anisotropic composites, it was deemed necessary to validate that differences observed between MFBs were a consequence of material variation, and not inherent in the experimental method. Therefore, MFBs were cut with a low speed diamond saw from a sheet of cast amorphous polycarbonate and tested. Standard size polycarbonate bendbars were also cut to determine if a size effect exists for a homogeneous polymer. Edges of the polycarbonate samples were lightly smoothed with 240 grit paper.
2.2.3. Injection molded chopped fiber PEEK: 30% chopped-carbon-fiber-reinforced poly(etheretherketone) CFRPEEK (450CA30– pellets received from ICI Chemicals) was injection molded (Dexter composites, Cleveland, Ohio) using a side gate. High modulus 7 micron diameter fibers (Hercules AS4) were used to reinforce the PEEK matrix. These bendbars were from the same batch of bendbars that were tested for standard size flexural properties (Mason, 1992).

To determine fiber orientation and distribution in the injection-molded bendbar, two bars were sectioned with a band saw into four equal sections (A,B,C,D) (Figure 2.3.). Each of these sections was cut in half either through the thickness or through the width with a slow speed saw (Buehler-Isomet) and diamond wafering blade (B111-4245, 5 x 0.015”). The sections were then sanded and polished using standard metallographic technique, and viewed under a dissecting scope (Bausch and Lomb) for global orientation, and with a reflected light microscope (Zeiss) for microstructural detail.

MFBs for flexural testing were cut from injection-molded bendbars as illustrated in Figure 2.3. One bendbar was cut into sections A, B, C, and D using a bandsaw. Each section was then cut through the width (in the X-Z plane, perpendicular to the Y axis) using a diamond blade on a low speed saw. As-cut Y-MFBs were approximately 1 x 6 x 30 mm. The edges of each MFB were lightly sanded with 240 grit carburundum paper. The surface MFBs, which were the first and the last cuts (and therefore may have been cut irregularly), were sanded to uniform dimensions only on the cut (not
Figure 2.3. Sectioning of injection-molded 30% CFRPEEK bendbars into Y and Z MFBs.
the molded surface) side. Another bendbar was also cut into sections A, B, C, and D. Each section was then cut through the thickness into Z-MFBs. Z-MFBs were cut in the X-Y plane perpendicular to the Z-axis. As cut Z MFBs were approximately 1 x 5 x 30 mm. Once again the surface sections were sanded to uniformity on the cut side if necessary. Y and Z MFBs were tested to failure using the 245 N load cell and the MTS extensometer. The edge MFBs were tested with the molded surface side down (in tension).

2.2.4. Density: The density of each of the fractured halves of the CFRPEEK Z MFBs was determined using Archimedes principle in accordance with ASTM standard D792, Specific Gravity and Density of Plastics by Displacement. A Mettler density determination kit was used with a Mettler AE163 microbalance. A weighing pan, bracket, beaker and gem holder were attached to the Mettler. Specimens were first weighed dry. The specimens were then conditioned by being immersed in boiling distilled water and then being placed, still in water, under vacuum (500 mmHg) for two hours to allow the materials to degas. This process enabled the water to spread on the surface of the specimen (which may have had surface irregularities) in order to avoid the formation of air bubbles which can distort results. Once the specimens were conditioned (in individual 12 x 75 mm polystyrene tubes), they were weighed. Each specimen was first weighed wet in the gem holder suspended in the 250 ml beaker filled with distilled water (temperature monitored). The weight was determined after
taring the Mettler to account for the weight of the suspension wire and gem holder. To find the saturated weight, the specimen was removed, the surface wiped with a laboratory tissue (Kimwipe) and weighed in the top pan. It was noted that the saturated weight and the dry weight were nearly identical (due to very little porosity in the specimens). Therefore, the calculations used to determine density were:

\[
\text{Density(sample)} = \\
(D\text{ry weight}/(D\text{ry weight} - \text{wet weight})) \times \text{Density(dist. H}_2\text{O)}
\]

where Density of distilled water at 24°C = .9973 g/cm³.

Density in a composite is also a function of the volume fraction of matrix material and the volume fraction of reinforcing material, carbon fibers:

\[
P_{\text{comp}} = P_m V_m + P_f V_f
\]

where \( P_m = \text{density of matrix (PEEK)} \)
\( V_m = \text{volume fraction of matrix} = (1 - V_f) \)
\( P_f = \text{density of fibers (Hercules AS4)} = 1.77 \text{ g/cm}^3 \)
\( V_f = \text{volume fraction of fibers} \)

The volume fraction of the fibers is calculated from

\[
V_f = 1/[1 + (P_f/P_m)(1/W_f - 1)]
\]

where \( W_f = \text{weight fraction of fibers} = 0.3 \)

2.2.5. Analysis of Flexural Testing Results:

Maximum flexural stress, strain at maximum stress, and bending modulus were calculated according to ASTM standard D790M. Strain was measured at maximum stress for consistency since the load deflection traces after the point of maximum stress was reached varied between
specimens. In addition, the fraction of strain that was due to plastic deformation processes was approximated using simple curve analysis. As illustrated in Figure 2.4a a plot of bending stress versus axial strain can be broken into components of elastic and plastic behavior. A key element of elasticity is the recovery of elastic strain once stress has been removed. This recovery is indicated by the dashed line. Therefore, the fraction of strain that is a result of plastic flow can be calculated by dividing the plastic strain by the total strain. The fraction of plastic strain encountered in the MFFs at the point of maximum stress was determined by analyzing the load-deformation curves as shown in Figure 2.4b.

Results of flexural testing were statistically analyzed using the BMDP Statistical Software package (1988 release). A brief description of how the software works is located in Appendix A. Also included in Appendix A are the instruction files and the data files created for use with the individual BMDP programs. Five BMDP programs were used.

The first program, DM (data manager), organized the data into a file that could be used in all other programs. This program was also used for preliminary data screening and the formation of data subsets. To compute descriptive statistics such as means, standard deviations and histograms, Program 2D was used. This program also enabled evaluation of the normality assumption that is required when using such statistics as T-tests and regression analysis.

Program 7D, One- and Two- Way Analysis of Variance with Data
a) Stress - Strain Curve

b) Load - Deformation Curve

Figure 2.4. Determination of the plastic fraction from a) stress-strain curves and b) load-deformation curves.
Screening was used primarily to determine significance between sample groups using both the student's T-test and ANOVA. The assumption of equality of variances between sample groups was tested with the Levene test. If this assumption was upheld then the T-test could be applied using pooled variances (and thus increasing the number of degrees of freedom). If the equality of variances assumption was invalid, then the T-test was applied using separate variances. Significance at the .05 level was determined using Bonferroni's correction for multiple comparisons. This conservative correction states that a .05 significance level is attained if $P < .05/N$, where $N$ is the number of comparisons being made.

To determine the effects that several factors (i.e. position of the MFB in the original bar) may have on the dependent variables (stress, strain, modulus), program 4V, Univariate and Multivariate Analysis of Variance, was used. The multivariate ANOVA was helpful in determining if there were any interactions between factors (such as specimen section (A,B,C,D), and position (edge or core)).

2.2.6. Scanning Electron Microscopy (SEM): The fracture surfaces of representative MFBs were analyzed with the SEM (JEOL 840, Dept. Macromolecular Science, Olin). The fractured ends of specimens were cut with a bandsaw (the surfaces protected with tape). The samples were then sonicated in distilled water for 5-10 minutes, and air dried. The specimens were mounted with the fractured surfaces facing up. Four to six specimens were glued (DUCO cement) to an aluminum
SEM stub. The specimens were coated with gold.

2.2.7. Residual Stresses: To determine if residual stresses were relieved upon cutting the MFBs and to determine an approximate magnitude of these stresses, a technique was employed using strain gages as indicated in Figure 2.5. Previously, strain gages have been successfully used in a layer removal technique to determine residual stresses in a plastic pipe (Chaoui et al., 1988). A single 120 ohm gage (Micro Measurements EA-13-125-BB-120) was bonded (H-bond 200) to the surface of an injection molded CFRPEEK bendbar as shown in Figure 2.5. This bar served as a control. Another CFRPEEK bendbar was gaged similarly. The gage on the control bendbar was hooked into a quarter bridge circuit using a strain gage conditioner (2120A, Measurements Group). The bridge was balanced and the gage then calibrated to ± 1000 microstrain. The gage on the other bendbar replaced the control gage in the circuit. Any difference (usually slight) between the output for the two gages was noted.

The ends of the test bendbar were then cut on a bandsaw so that the gaged section could be cut on a diamond saw. Once the ends were cut, the output of the gage was tested against the control gage. Any change in strain was noted. The lead wires were removed from the test bendbar. On the diamond saw, approximately 1 mm (similar to the depth of a MFB) was cut from the bendbar. The resulting slice, with the gage still attached, was air dried, and the lead wires reattached to the gage. Once again the output of this gage was compared with
Figure 2.5. Strain gage method to determine residual stresses in the I-M 30% CFRPEEK bendbar.
that of the control gage. Any change in strain was noted. The block that remained after slicing was then gaged and the entire process repeated. Strain measurements were obtained for three sequential slices through the thickness of the bendbar. To consider possible viscoelastic effects, each slice was remeasured after two weeks.

2.2.8. Ultrapek Composites: An Ultrapek composite was formed by compression molding comingled fiber, AS4 carbon/Ultrapek (Acromed). The fiber was puffed up into a fuzzball and placed in the mold. Although, the intent of this process was the formation of a homogeneous composite, the result resembled a composite laminate where the composite is somewhat homogeneous in the directions parallel to the platens but significantly weaker in the direction perpendicular to the platens (due to extensive fiber breakage). The need to examine the mechanical properties of the freeform composite was determined to be twofold. First to establish what the mechanical properties were for this unorthodox composite, and secondly, to evaluate the reproducibility of these mechanical properties from lot to lot, and even within the same block. To do this, MFBs were used.

Miniflexbars (1 x 10 x 28 mm) were cut from the first consolidated freeform Ultrapek composite and tested in 3 point bending. Grooves originally molded in the 5 mm x 28 mm x 120 mm composite were removed by sanding. MFBs were cut in two directions parallel to the molding platens (Y,Z) and in one direction
perpendicular to the molding platens (X) as indicated in Figure 2.6.

MFBs were also machined from a 3/4" thick slab of the freeform Ultrapek composite (lot # 3859) which was approximately 10" in diameter. All specimens were cut parallel to the molding platens. Specimens of various dimensions and from multiple locations in the composite block were flex tested to examine effects of specimen size and homogeneity of the material.

In comparison to the freeform Ultrapek composite, a A 0/90 layup of 88 laminate cloths of continuous carbon fiber reinforced Ultrapek was compression-molded at Dexter composites. A section from the middle portion of the block, which was well consolidated, was received from Acromed. Y and Z MFBs were cut. The MFBs were mechanically tested using the big load cell (980 N max load).
Figure 2.6. Schematic showing how the freeform Ultrapek composites were formed, and the directions that samples were cut.
2.3. Results

2.3.1. Polycarbonate: Results of testing polycarbonate MFBs and standard size bendbars are shown in Table 2.2. No significant difference was found between strength at 5% strain, strain or modulus. An increase was observed however for both 5% strength and strain. This may be indicative of the size affect associated with brittle materials. The MFBs have a smaller area for flaws to be found which will cause early failure of the specimens. This correlates with similar testing of Plexiglass 1 x 10 x 30 mm samples compared with Plexiglass 3 x 10 x 60 mm (Brown and Bargar, 1984). The small standard deviation for the results of the bigger bars indicates slight variation between specimens. An increase in variation of approximately 2% is observed for the results of testing the MFBs. This may be attributed to either experimental design or material variation. Either way, the slight standard deviation from the mean supports the hypothesis that there was only a very small amount of error associated with the experimental set-up.

2.3.2. Fiber Orientation: The general pattern of fiber distribution in the 6 x 12 x 120 mm bendbar is schematically illustrated in Figure 2.7. The left figure is the top view representing fiber flow viewed in the X-Y plane, and the right figure is the side view of the center of the bar representing fiber flow viewed in the X-Z plane. The micrographs in Figure 2.8 depict the fiber orientation observed in the X-Y plane. Similar observations were also evident in the X-Z
Table 2.2. Flexural testing results for standard size polycarbonate bendbars and polycarbonate MFBs. Standard deviations in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Stress (%)</th>
<th>Strain (%)</th>
<th>Mod (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFBs</td>
<td>7</td>
<td>94.5(1.0)</td>
<td>93.9(0.8)</td>
<td>5.64(.43)</td>
<td>2.87(.03)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>100.8(2.7)</td>
<td>96.1(3.2)</td>
<td>6.26(.26)</td>
<td>2.80(.12)</td>
</tr>
<tr>
<td></td>
<td>p&lt;.05</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>
Figure 2.7. Schematic of fiber orientation in the I-M 30%CFRPEEK bendbar.
plane.

In section A (Figure 2.7), where the gate is located, it can be seen that fiber flow patterns begin at the gate and radiate outward. Since the gate was located on the left and not the top, the center of the transition region from transverse fibers to fully aligned fibers was shifted towards the right, away from the gate, allowing more fibers to be angled towards longitudinal alignment than to transverse alignment for the side of the bar away from the gate. The corners of section A (Figure 2.8a) consisted of transverse fibers, similar to what was seen in section D.

In the lower part of section A, alignment of the fibers at the edges of the bar was just beginning. In sections B and C, fibers were predominantly aligned at the surfaces with the edge away from the gate having a thicker layer of oriented fibers (Figure 2.8b) than the edge near the gate.

In the core regions of these sections, the flow patterns were curvilinear with alternating flow lines of longitudinal and transverse fibers (Figure 2.8c). A transition region from edge (fully aligned fibers) to core (transverse fibers) was apparent as well (Figure 2.2d). Once again these regions were shifted to the right, the gated side of the bar.

Section D had a microstructure that was similar to section A without the gate. The corners and bottom of section D were dominated by transverse fibers. The upper region of section D had flow lines and alignment of fibers similar to the lower region of
Figure 2.8a. Light micrograph of fiber orientation in the upper corner of section A. Fibers are predominantly transverse.

Figure 2.8b. Light micrograph of fiber orientation at the edge away from the gate in section B. Although most of the fibers are oriented parallel to the edge, there are some fibers that are transverse.
Figure 2.8c. Light micrograph of fiber orientation in the center of section B. Notice the alternating pattern of transverse and longitudinal fibers.

Figure 2.8d. Light micrograph of fiber orientation in section C showing the angled alignment of fibers.
section A, but more extensive.

2.3.3. Density: The results of the density experiments are shown in Table 2.3. The average density of the CFRPEEK Z MFBs was 1.4140 g/cm³. The density of the Z MFBs from section D was significantly lower compared to Z bars in section B and C. This may be attributed to a decrease in the number of fibers or to a decrease in matrix crystallinity which may be associated with the fibers.

To determine $V_f$ and $P_m$ of the injection molded bendbar based on the mean value of density for the Z MFBs (Table 2.3.) the volume fraction of the fibers was .2397 and the density of the PEEK matrix was 1.3018. However, the density of PEEK is dependent upon the volume fraction of crystalline material and the volume fraction of amorphous material. This is calculated from

$$P_m = P_A V_A + P_C V_C$$

Where

$v_A = \text{volume fraction of amorphous PEEK}$
$v_C = \text{volume fraction of crystalline PEEK} = 1 - v_A$
$P_A = \text{density of amorphous PEEK} = 1.2626 \text{ g/cm}^3$ (Blundell and Osborn, 1983)
$P_C = \text{density of crystalline PEEK} = 1.4006 \text{ g/cm}^3$ (Blundell and Osborn, 1983)

Substituting $P_m$ from above the volume fraction of amorphous material in the composite is found to be 0.7159, and the volume fraction of crystalline material to be 0.2841. This is a reasonable result since it was determined that the skin of the CFRPEEK injection molded flexbar in the center has a crystallinity of 0.3066 (Mason, 1990).

The differences in density observed in Table 2.3. could be a
consequence of a change in matrix crystallinity or in a change in the fiber volume fraction.

2.3.4. Flexural Testing: The results of flexural testing of the Y and Z bars are indicated in Table 2.4. There was not a significant difference between the Y and Z bars for flexural strength, strain or modulus. This is understandable since the microstructure was similar in both directions. Therefore, to increase sample size, the Y bars were combined with the Z bars. The overall combined flexural strength of the MFBs was 280 MPa. This strength was approximately 10 \% less than the flexural strength found for the intact injection molded bendbars (Mason et al., 1990). A decrease in strain and increase in modulus was also observed in comparing the flexural properties of the MFBs with the standard bars. This difference, however, will be explained.

The hypothesis was that the flexural properties of an MFB will be affected by its location within the bendbar due to variation in microstructure. Based on the previous density and microstructural analysis, it was concluded that the ends of the bendbar were microstructurally different than the middle of the bendbar. Therefore, MFBs from the end sections A and D were lumped together for statistical analysis, and the MFBs from the middle sections B and C were lumped together. In Table 2.5, the flexural results of the MFBs in sections A&D are compared with the B&C MFBs. As Table 2.5 indicates, the MFBs located in sections B and C were stronger and
Table 2.3. Density of Z CFRPEEK MFBs

<table>
<thead>
<tr>
<th>MFBs</th>
<th>N</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>32</td>
<td>1.4140 (0.0014)</td>
</tr>
<tr>
<td>AZ</td>
<td>8</td>
<td>1.4141 (0.0019)</td>
</tr>
<tr>
<td>BZ</td>
<td>8</td>
<td>1.4145 (0.0009)</td>
</tr>
<tr>
<td>CZ</td>
<td>8</td>
<td>1.4146 (0.0019)</td>
</tr>
<tr>
<td>DZ</td>
<td>8</td>
<td>1.4129 (0.0009)</td>
</tr>
</tbody>
</table>

*DZ statistically significant compared to groups BZ (p<.005) and CZ (p<.02)

Table 2.4. Flexural stress, strain and modulus for All (Y and Z) MFBs, only Y MFBs and only Z MFBs. Values for Standard were those determined for the standard size 30% CFRPEEK MFB (Mason, 1992).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All MFBs</td>
<td>65</td>
<td>280.02 (37.93)</td>
<td>3.21 (0.54)</td>
<td>13.50 (3.05)</td>
</tr>
<tr>
<td>Y MFBs</td>
<td>33</td>
<td>281.78 (29.80)</td>
<td>3.27 (0.56)</td>
<td>13.65 (2.90)</td>
</tr>
<tr>
<td>Z MFBs</td>
<td>37</td>
<td>278.20 (45.24)</td>
<td>3.14 (0.52)</td>
<td>13.34 (3.24)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Standard</td>
<td>10</td>
<td>314.00 (3.80)</td>
<td>2.28 (0.08)</td>
<td>18.10 (0.45)</td>
</tr>
</tbody>
</table>
Table 2.5. Flexural stress, strain and modulus for various subgroups of the Y and Z 30% CFRPEEK MFBs. Values for Standard were those determined for the standard size 30% CFRPEEK MFB (Mason, 1992).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>33</td>
<td>266.93 (35.25)</td>
<td>3.58 (0.48)</td>
<td>11.82 (2.51)</td>
</tr>
<tr>
<td>BC</td>
<td>32</td>
<td>293.52 (36.30)</td>
<td>2.82 (0.26)</td>
<td>15.24 (2.56)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-value</td>
<td>.001</td>
<td>.001</td>
</tr>
<tr>
<td>AD away</td>
<td>15</td>
<td>291.84 (23.10)</td>
<td>3.33 (0.36)</td>
<td>13.50 (1.99)</td>
</tr>
<tr>
<td>BC away</td>
<td>16</td>
<td>305.87 (28.09)</td>
<td>2.74 (0.21)</td>
<td>16.18 (2.11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-value</td>
<td>NS</td>
<td>.005</td>
</tr>
<tr>
<td>AD near</td>
<td>16</td>
<td>244.47 (30.86)</td>
<td>3.78 (0.47)</td>
<td>10.31 (2.03)</td>
</tr>
<tr>
<td>BC near</td>
<td>14</td>
<td>280.38 (42.94)</td>
<td>2.88 (0.31)</td>
<td>14.25 (2.88)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-value</td>
<td>.005</td>
<td>.001</td>
</tr>
<tr>
<td>AD edge</td>
<td>12</td>
<td>272.64 (38.72)</td>
<td>3.39 (0.35)</td>
<td>12.20 (2.68)</td>
</tr>
<tr>
<td>BC edge</td>
<td>12</td>
<td>324.46 (20.62)</td>
<td>2.65 (0.16)</td>
<td>17.19 (1.44)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-value</td>
<td>.001</td>
<td>.001</td>
</tr>
<tr>
<td>AD core</td>
<td>21</td>
<td>263.67 (33.65)</td>
<td>3.69 (0.51)</td>
<td>11.60 (2.44)</td>
</tr>
<tr>
<td>BC core</td>
<td>20</td>
<td>274.95 (30.59)</td>
<td>2.92 (0.26)</td>
<td>14.08 (2.39)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-value</td>
<td>NS</td>
<td>.001</td>
</tr>
<tr>
<td>Standard</td>
<td>10</td>
<td>314.00 (3.80)</td>
<td>2.28 (0.08)</td>
<td>18.10 (0.45)</td>
</tr>
</tbody>
</table>
stiffer on average than the bars located in sections A and D.

Fiber orientation analysis in the standard size bendbar also illuminated differences in microstructure for those bars located away from the gate compared with those bars located near the gate. Specifically, for the B&C bars located away from the gate an increase in strength, although not significant, a significant decrease in strain, and a significant increase in modulus were observed compared to the A&D bars located away from the gate. For the B&C bars located near the gate strengths, strains and moduli were significantly different compared to the A&D bars located near the gate.

The third major grouping of common microstructural features was for the MFBs located at the edges (surface) of the intact bendbars, compared to those MFBs located in the core of the intact bendbar. For the bars located at the edge of sections B and C and bars located at the edge of sections A and D a significant difference was also found. This can be accounted for by the fiber alignment at the surface that was observed in the middle of the injection molded bendbar that was not observed at the far ends of the bendbar. The core bars in sections A and D compared to the core bars in sections B and C tended to be less strong, though not significant, and less stiff, which is significant.

Based on microstructure, it was thought that the location of an MFB away or near the gate in the end sections, A&D, would have an influence on the flexural properties of the MFB. Flexural results comparing MFBs away from the gate with those near the gate are given
in Table 2.6. A significant difference was found for strength, strain and modulus (Table 2.6). This is consistent with the fiber orientation in section A being especially influenced by the gate. Closer to the gate the fibers are oriented randomly and further away the fibers become more aligned and begin the flow pattern observed in the lower part of section A and the upper part of section D. Also, areas of transverse fiber orientation in section D were located primarily in the corner and side that was closest to the gate.

Comparing the edge and core bars within sections A&D, a significant difference was not found (Table 2.6). This was a consequence of the fibers not being aligned at the edges of parts of sections A and D. This also gives evidence that the surface finish, which is present on the edge MFBs in section A&D, may not be important for increasing the strength of the composite.

The influence of the gate (away or near) and position (edge or core) on flexural properties for the middle sections B&C was also examined. In Table 2.7 results from comparing MFBs located away from the gate compared to the MFBs located near the gate were not significant. The MFBs located away from the gate however, tended to be stronger and stiffer than those located near.

It was expected that differences in flexural properties between edge bars in sections B&C would be different from the core bars because of the obvious differences in fiber alignment. Shown in Table 2.7 a significant increase in strength and stiffness and a significant decrease in strain was found between the edge and core
Table 2.6. Flexural stress, strain and modulus for the AD CFRPEEK MFBs. Values for Standard were those determined for the standard size 30% CFRPEEK MFB (Mason, 1992).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>13</td>
<td>266.93 (35.25)</td>
<td>3.58 (0.48)</td>
<td>11.82 (2.51)</td>
</tr>
<tr>
<td>AD away</td>
<td>15</td>
<td>291.84 (23.10)</td>
<td>3.33 (0.36)</td>
<td>13.50 (1.99)</td>
</tr>
<tr>
<td>AD near</td>
<td>16</td>
<td>244.47 (30.86)</td>
<td>3.78 (0.47)</td>
<td>10.31 (2.03)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.001</td>
<td>.01</td>
<td>.001</td>
</tr>
<tr>
<td>AD edge</td>
<td>12</td>
<td>272.64 (38.72)</td>
<td>3.39 (0.35)</td>
<td>12.20 (2.68)</td>
</tr>
<tr>
<td>AD core</td>
<td>21</td>
<td>263.67 (33.65)</td>
<td>3.69 (0.51)</td>
<td>11.60 (2.44)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Standard</td>
<td>10</td>
<td>314.00 (3.80)</td>
<td>2.28 (0.08)</td>
<td>18.10 (0.45)</td>
</tr>
</tbody>
</table>

Table 2.7. Flexural stress, strain and modulus for the BC CFRPEEK MFBs. Values for Standard were those determined for the standard size 30% CFRPEEK MFB (Mason, 1992).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>12</td>
<td>293.52 (36.30)</td>
<td>2.82 (0.26)</td>
<td>15.24 (2.56)</td>
</tr>
<tr>
<td>BC away</td>
<td>16</td>
<td>305.87 (28.09)</td>
<td>2.74 (0.22)</td>
<td>16.18 (2.11)</td>
</tr>
<tr>
<td>BC near</td>
<td>14</td>
<td>280.38 (42.94)</td>
<td>2.88 (0.31)</td>
<td>14.25 (2.88)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>BC edge</td>
<td>12</td>
<td>324.46 (20.62)</td>
<td>2.65 (0.16)</td>
<td>17.19 (1.44)</td>
</tr>
<tr>
<td>BC core</td>
<td>20</td>
<td>274.95 (30.59)</td>
<td>2.92 (0.26)</td>
<td>14.08 (2.39)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.001</td>
<td>.005</td>
<td>.005</td>
</tr>
<tr>
<td>Standard</td>
<td>10</td>
<td>314.00 (3.80)</td>
<td>2.28 (0.08)</td>
<td>18.10 (0.45)</td>
</tr>
</tbody>
</table>
bars in sections B&C. The aligned surface fibers in sections B and C provided extra strength, since the fibers were aligned perpendicular to the fracture plane, whereas in the core region the fibers were either at an angle, or parallel to the fracture plane. Importantly, the edge bars in sections B and C compared to the uncut injection molded bar had strengths, strains and stiffnesses that were similar. Experimentally determined flexural properties from three point bend testing are dominated by the mechanical properties at the surface of the specimen, particularly underneath the loading nose. The location of the B and C edge bars corresponded to the tested surface of the intact injection-molded bend bar. This can explain why the overall average values for strength, strain and modulus of the MFBs are less than the averages of the intact injection-molded bar.

In Figure 2.9, flexural stress for each individual MFB is plotted with respect to position of the MFB in the uncut bendbar. Graphs for the Y MFBs are on the right, and graphs for the Z MFBs are on the left. The x-axis indicates position, and the y-axis stress in MPa. There is one graph for each section, A, B, C, and D. The MFBs that were cut closest to the gate are located at the far left of the x-axis. The position of the two edge bars from sections A, B, C and D correspond to the edges of the graph. Flexural stresses in the range of 180 to 360 MPa were observed. The value of 314 MPa represents the published value for the uncut bendbars (Mason et al., 1992).

In each section it is seen that flexural stress increases with
Figure 2.9. Trends in ultimate flexural stress with position in the I-M 30%CFRPEEK bendbar.
the minibars that are cut further away from the gate. This corresponds with the fibers being increasingly aligned the further away from the gate. In section C, the flexural stress of the edge bars are greater than the average flexural strength of the standard size bar. This is also true for the edge bars located away from the gate in B. An edge/core trend is not seen for sections A or D. It can also be seen that the overall strengths in sections A and D are less than in sections B and C.

For the 2 MFBs, the four graphs on the far left in Figure 2.9 plot position vs. maximum flexural strength of the MFBs which were cut from the gated side of the uncut injection molded bar. And the four graphs on the right plot position vs maximum flexural strength of the MFBs which were cut away from the gated side of the bar. The edge bars are at the extreme position on the graph and the core bars are the inner positions. Sections B, C, and D show very clearly the effect of the edge fiber alignment on increasing the strength of the bar.

These results indicate that the MFBs are sensitive to local microstructural differences described globally as end sections (A&D) or middle sections (B&C), away from the gated side or near the gated side, and edge or core. In many of the same sample groups, both stress and modulus were significantly different. This implies that both elastic behavior (as described by modulus) and plastic behavior (as described by ultimate stress) of the composite are effected by local microstructure and can be detected by the MFBs.
Means and standard deviations for the percent plastic strain are listed in Table 2.8. The data from sample groups All MFBs, Y MFBs and Z MFBs were normally distributed. Since the plastic fraction was significantly different between the Y MFBs and the Z MFBs these sample groups could not be combined.

Results from analysis of the plastic fraction and relating this to microstructural differences are given in Table 2.9. For the Y MFBs, significance was found between A&D and B&C MFBs, between A&D edge and B&C edge MFBs, and between A&D core and B&C edge MFBs. For both Y and Z MFBs the difference between sections is important in determining the degree of plasticity (the fraction plastic being higher in sections AD then sections BC). Also edge and core location can influence the plastic fraction. Once again, these effects can be related back to local microstructural differences including fiber orientation and location.

2.3.5. ANOVA: The results of Multivariate ANOVA analysis were used to further examine the effects that microstructural differences have on resulting flexural strengths, strains, modulus and fraction plasticity. The factors considered included MFB (Y or Z), Section (A&D or B&C), Position (edge or core) and Gate (away or near). Density was not considered as a factor in these calculations, since density is interrelated with all of the above. Results are displayed in Table 2.10 for strength, strain, modulus and fraction plasticity. The ANOVA for stress demonstrated that Section, Gate and Position
Table 2.8. The plastic fraction of the Y&Z MFB stress-strain curve.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Plastic Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y&amp;Z MFBs</td>
<td>65</td>
<td>.328 (.045)</td>
</tr>
<tr>
<td>Y MFBs</td>
<td>33</td>
<td>.345 (.039)</td>
</tr>
<tr>
<td>Z MFBs</td>
<td>32</td>
<td>.310 (.045)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.0016*</td>
</tr>
</tbody>
</table>

Table 2.9. Plastic fraction of the stress-strain curves for various subsets of CFRPEEK MFBs.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Y MFBs Fraction Plastic</th>
<th>N</th>
<th>ZMFBs Fraction Plastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&amp;D</td>
<td>17</td>
<td>.368 (.030)</td>
<td>16</td>
<td>.332 (.039)</td>
</tr>
<tr>
<td>B&amp;C</td>
<td>16</td>
<td>.321 (.034)</td>
<td>8</td>
<td>.269 (.040)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.0039</td>
<td></td>
<td>.0002</td>
</tr>
<tr>
<td>A&amp;D core</td>
<td>13</td>
<td>.376 (.026)</td>
<td>8</td>
<td>.337 (.048)</td>
</tr>
<tr>
<td>B&amp;C core</td>
<td>13</td>
<td>.328 (.031)</td>
<td>8</td>
<td>.307 (.029)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>A&amp;D edge</td>
<td>4</td>
<td>.339 (.026)</td>
<td>8</td>
<td>.328 (.031)</td>
</tr>
<tr>
<td>B&amp;C edge</td>
<td>3</td>
<td>.293 (.035)</td>
<td>8</td>
<td>.270 (.042)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.0083</td>
<td></td>
<td>.0056</td>
</tr>
<tr>
<td>A&amp;D core</td>
<td>13</td>
<td>.376 (.026)</td>
<td>8</td>
<td>.337 (.048)</td>
</tr>
<tr>
<td>B&amp;C edge</td>
<td>3</td>
<td>.293 (.035)</td>
<td>8</td>
<td>.270 (.042)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.0108</td>
<td></td>
<td>.0001</td>
</tr>
<tr>
<td>A&amp;D core</td>
<td>13</td>
<td>.376 (.026)</td>
<td>8</td>
<td>.337 (.048)</td>
</tr>
<tr>
<td>A&amp;D edge</td>
<td>4</td>
<td>.339 (.026)</td>
<td>8</td>
<td>.328 (.031)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>B&amp;C core</td>
<td>13</td>
<td>.328 (.031)</td>
<td>8</td>
<td>.307 (.029)</td>
</tr>
<tr>
<td>B&amp;C edge</td>
<td>3</td>
<td>.293 (.035)</td>
<td>8</td>
<td>.270 (.042)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.0640</td>
<td></td>
<td>.0652</td>
</tr>
</tbody>
</table>
Table 2.10. Results from multivariate ANOVA analysis examining the effects of MFB, Section, Gate and Position on flexural stress, strain, and modulus as well as on plastic fraction.

<table>
<thead>
<tr>
<th>VARIATION</th>
<th>STRESS</th>
<th>STRAIN</th>
<th>MOD</th>
<th>PLASTIC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MAIN EFFECT</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFB (Y or Z)</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>*</td>
</tr>
<tr>
<td>Section (A&amp;D or B&amp;C)</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Gate (Away or Near)</td>
<td>*</td>
<td>*</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Position (Edge or Core)</td>
<td>*</td>
<td>*</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td><strong>TWO FACTOR INTERACTIONS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFB-Section</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>MFB-Gate</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>MFB-Position</td>
<td>*</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Section-Gate</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Section-Position</td>
<td>*</td>
<td>NS</td>
<td>*</td>
<td>NS</td>
</tr>
<tr>
<td>Gate-Position</td>
<td>NS</td>
<td>*</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td><strong>THREE FACTOR INTERACTIONS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFB-Section-Gate</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>MFB-Section-Position</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>MFB-Gate-Position</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Section-Gate-Position</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td><strong>FOUR FACTOR INTERACTIONS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFB-Section-Gate-Position</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

NS - Not Significant  
* - Significant at p<.05
were all significant factors in determining outcome, however MFB (Y or Z) was not. Also evident was the interaction between MFB and Position and between Section and Position. Three and four factor interactions are not significant. If interaction is not significant, then the results of the tests on the main effects are meaningful. However, if interaction should be significant, then only those tests on the main effects that turn out to be significant are meaningful. Nonsignificant main effects in the presence of interaction might well be a result of masking and dictate the need to observe the influence of each factor at fixed levels of the other (Walpole and Myers, 1989). The main effects that are significant for strain include Section, Gate and Position. The only two factor interaction is between gate and position. For modulus once again Section, Gate and Position are significant. Three two-factor interactions exist: MFB-Position, Gate-Position and Section-Position. The first two of these were the same for stress. Only the fraction plastic variable has different main effects which are significant MFB, Section and Position. Two factor interactions are not significant.

To examine why the two factor interactions exist, once again we must resort to microstructure. For stress, strain and modulus all two-factor interactions occur between section, gate or MFB and position. Take for example the interaction for stress and modulus between MFB and Position. Position indicates whether the MFB is a located at the edge or core. Only those MFBs that contain an
original external surface are considered edge. The Y MFBs were cut such that only two MFBs per section are labelled as edge. The seven other MFBs per section are core. In contrast the Z MFBs consisted of an equal number of edge and core MFBs per section, with two core MFBs in the middle of two edge MFBs. The transition between edge (where fibers are presumably aligned) and core is much smaller for the Z MFBs as compared to the Y MFBs.

2.3.6. Scanning Electron Microscopy: The fracture surfaces of MFBs which were located from representative positions (such as edge and core) were examined. An SEM micrograph of an edge Z MFB is shown in Figure 2.10a. As expected the majority of the fibers are oriented in the X-Y plane. The micrograph in Figure 2.10b is representative of transverse orientation observed in most core MFBs. The degree of transverse fiber orientation observed in fracture surfaces of core MFBs varied with position. An interesting observation, which was noted with almost all of the MFB fracture surfaces looked at, was the transition between coated fibers on the compression side and uncoated fibers on the tension side. This is illustrated for an edge MFB in Figure 2.11 and Figure 2.10c. SEM micrographs of core MFBs also show the transition from coated to uncoated fibers. However, there is an increased amount of matrix yielding apparent (2.10d).

SEM analysis was also used in an attempt to understand the stress strain curves of the MFBs. Shown in Figure 2.12a is a stress strain curve of a MFB that failed catastrophically. In Figure 2.12b,
Figure 2.10a. SEM micrograph illustrating carbon fiber orientation in an edge MFB (CZ1-compression side of the fracture surface).

Figure 2.10b. SEM micrograph illustrating a region of carbon fiber orientation in a core MFB (CZ7-tension side of the fracture surface).
Figure 2.10c. SEM micrograph illustrating matrix ductility in a core MFB (CZ7-tension side of the fracture surface).

Figure 2.10d. SEM micrograph illustrating the transition from uncoated fibers on the tensile side to coated fibers on the compressive side (CZ1). This was typical for many MFBs.
and uncoated fibers are observed. Surface from the tensile to the compressive side (B21). Both coated

Figure 2.11. SEM montage indicating the appearance of the fracture
Figure 2.12. Stress-strain curves from flexural testing 30%CFRPEEK MFBs indicating two typical types of observed failure: a) catastrophic failure and b) non-catastrophic or stepwise failure.
a stress strain curve of an MFB that did not fail catastrophically is exhibited. The fracture tail in Figure 2.12b that was associated with several MFBs was hypothesized to be due to a transition between regions of fiber orientation, which could slow down a fast crack. Transitions from aligned fibers as illustrated in Figure 2.10a to transverse fibers such as in Figure 2.10b were observed for many core MFBs, as well as a few edge MFBs. However it can not be concluded that fiber orientation transitions will automatically result in a fracture tail. An interesting coincidence is that the fracture tails are observed with all BZ, CZ, and DZ MFBs in positions 6 and 7 (which are away from the gate), as opposed to positions 2 and 3 (which are near the gate). In fact the microstructure of a CZ MFB located in position 2 was more similar to that of the MFB located at position 1 than position 7. This supports the light micrographs which indicated that the zones of fiber alignment was thicker at the surface away from the gate than near the gate.

2.3.7. Residual Stresses: The results of residual stress measurements are given in Table 2.11. The data shown that slices #1 and #2 experienced positive strain when cut, and slice #3 experienced negative strain. The average flexural modulus of the BC edge MFBs for slice #1 and the average flexural modulus of the BC core MFBs for slices #2 and #3, were used in Hooke's law (σ=Eε) to determine approximate axial stress relieved. As seen in Table 2.11, the outer two slices of the bendbar were in residual compression, and the core
Table 2.11. Residual Stress Measurement Results

<table>
<thead>
<tr>
<th></th>
<th>Depth (mm)</th>
<th>μstrain</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice #1 -</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reading 1</td>
<td>1.2</td>
<td>730</td>
<td>12.56</td>
</tr>
<tr>
<td>Reading 2</td>
<td></td>
<td>750</td>
<td>12.90</td>
</tr>
<tr>
<td>Slice #2 -</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reading 1</td>
<td>1.2</td>
<td>1650</td>
<td>23.23</td>
</tr>
<tr>
<td>Reading 2</td>
<td></td>
<td>1640</td>
<td>23.09</td>
</tr>
<tr>
<td>Slice #3 -</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reading 1</td>
<td>0.9</td>
<td>-250</td>
<td>-3.52</td>
</tr>
<tr>
<td>Reading 2</td>
<td></td>
<td>-420</td>
<td>-5.91</td>
</tr>
</tbody>
</table>
was in residual tension.

The impact of these released residual stresses on the values of MFB flexural strength are unknown. Although values have been recorded in Table 2.11, the absolute magnitudes can only be used as guides due to the assumptions involved in calculating the stress. These assumptions include: 1) stress is only relieved in the axial direction  2) the gages are aligned perfectly with the axis (this is difficult since there is a slight bend in the bar)  3) the stress can be calculated using Hooke's law. Also the viscoelastic nature of the material is unknown. Despite these assumptions it can be concluded that there are residual stresses, that may affect the flexural properties of the CFRPEEK injection molded bendbar. These stresses may account for some of the differences observed between MFBs, or between the overall average strength of the MFBs and the intact bendbar.

2.3.8. Ultrapak Composite: Results from testing MFBs from the Ultrapak freeform composites are shown in Table 2.12. Anisotropy in the flexural properties, especially strength, of the small freeform Ultrapak composite was observed between all three directions, although most significantly between those MFBs which were cut parallel to the platens and those cut perpendicular. A significant amount of scatter within specimen groups was also observed, indicating inhomogeneity. The Z MFBs from the small freeform block had a much greater strength than the Z MFBs from the large freeform
block. It is most likely that the large difference was a result of less-than-optimal processing. In comparison, the flexural strength of the [0/90] fabric Ultracek composite was significantly greater than either of the Ultracek freeforms.

Results of testing bendbars of various dimensions from the large freeform Ultracek composite are shown in Figure 2.12 (Table 2.13). This figure clearly illustrates the wide variation both between and within specimen groups. This is evidence of marked inhomogeneity. A closer examination showed that the MFBs had the most scatter in the data, the highest maximum strain and the lowest modulus. The moduli calculated for a few of the MFBs were low enough to possibly indicate matrix failure. The 1x25x60 mm flexbars with a 40:1 span were the weakest. This may be due to the wide span which can act as a flaw finder. Because of the larger span, more flaws or defects are available to cause an earlier failure.

To examine the effect of width on flexural properties, the 3x10x75 mm (16:1) and the 3x25x60 mm (16:1) flexbars were compared. The greatest strength was associated with the wider bars. The strain to failure of the 10 mm wide bars was also the lowest of all of the groups. The greater strength of the 25 mm wide bars may be due to the greater cross-sectional area between the supports.

Looking at the fracture surfaces of the freeform composites, it was observed that in all of the groups, most of the bars did not break directly under the nosepiece (the area of maximum stress), rather the fracture ran along fiber/matrix flow lines. This may
indicate either poor adhesion of the matrix to the fiber or that fracture was following a fiber avoidance mode, similar to what was observed in the chopped fiber composites. Very rarely did the bars break catastrophically. All of them had an initial failure, which usually occurred before the maximum strength had been reached.

From data in Table 2.12, a comparison between the freeform composites and other continuous fiber composites can be made. The freeform composites were found to have lower flexural strengths and moduli than other continuous fiber reinforced Ultracek composites. Table 2.12 shows that between the small and large freeform composites, the small freeform was the strongest. However, this composite only had a little under half of the strength of the unidirectional composite tested in the fiber direction. A more reasonable comparison of this composite was with the [0/90] Ultracek fabric composite. The small freeform however, was still weaker. In fact, the flexural properties of either the freeform MFBs (Table 2.12) or other dimensioned freeform specimens (Table 2.13), were similar to that observed for 30% chopped fiber reinforced Ultracek.

Compression molding a composite laminate is an art and science that requires multiple parameters to be optimized in order for a reliable part to be produced (Ishida, 1988). Without optimized conditions, flaws such as inadequate fiber/matrix bonding and pores can be introduced. In addition, as was discussed for the PEEK composites, processing conditions will substantially effect the morphology of the Ultracek matrix in the composite, i.e. the percent
Table 2.12. Flexural test results for Ultrapak freeform composite HFBs. Literature values for continuous fiber Ultrapak and chopped fiber Ultrapak are also given for comparison (SASF, 1989). Standard deviations are in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Small Freeform</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>311.3 (43.7)</td>
<td>2.9 (0.4)</td>
<td>15.7 (2.6)</td>
</tr>
<tr>
<td>Y</td>
<td>704.0 (82.0)</td>
<td>3.0 (0.6)</td>
<td>32.6 (6.2)</td>
</tr>
<tr>
<td>Z</td>
<td>801.3 (54.7)</td>
<td>2.7 (0.3)</td>
<td>48.8 (2.5)</td>
</tr>
<tr>
<td><strong>Large Freeform</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>263.3 (108.1)</td>
<td>3.2 (1.3)</td>
<td>13.7 (6.7)</td>
</tr>
<tr>
<td><strong>0/90 Fabric</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>971.1 (76.4)</td>
<td>2.7 (0.1)</td>
<td>37.9 (4.3)</td>
</tr>
<tr>
<td>Z</td>
<td>1035.4 (213.0)</td>
<td>3.0 (0.7)</td>
<td>42.7 (4.8)</td>
</tr>
<tr>
<td><strong>Ultrapak (KR-4178)</strong></td>
<td>126</td>
<td></td>
<td>3.8</td>
</tr>
<tr>
<td><strong>Ultrapak/30% carbon</strong></td>
<td>399</td>
<td></td>
<td>24.1</td>
</tr>
<tr>
<td><strong>Ultrapak/continuous fiber carbon (0°)</strong></td>
<td>1758</td>
<td></td>
<td>112.4</td>
</tr>
</tbody>
</table>

Table 2.13. Flexural test results for Ultrapak freeform composites of various dimensions. All samples tested with a 16:1 span:depth ratio unless noted (* 40:1 span:depth). Standard deviations in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 x 10 x 75 mm</td>
<td>261.0 (61.2)</td>
<td>1.6 (0.3)</td>
<td>21.0 (3.2)</td>
</tr>
<tr>
<td>3 x 25 x 60 mm</td>
<td>380.7 (73.0)</td>
<td>2.7 (0.3)</td>
<td>20.1 (3.2)</td>
</tr>
<tr>
<td>*1 x 25 x 60 mm</td>
<td>192.1 (57.3)</td>
<td>1.9 (0.3)</td>
<td>14.7 (2.7)</td>
</tr>
<tr>
<td>1 x 25 x 50 mm</td>
<td>345.7 (82.1)</td>
<td>3.0 (0.2)</td>
<td>20.2 (10.3)</td>
</tr>
<tr>
<td>1 x 5 x 30 mm</td>
<td>287.9 (121.8)</td>
<td>3.8 (1.3)</td>
<td>12.8 (7.4)</td>
</tr>
</tbody>
</table>
Figure 2.13. Flexural stress, strain and modulus of Ultrapek freeform composite specimens of various dimensions. Depth x width dimensions are given in millimeters.
crystallinity and the type of crystallites. The processing criteria required for PEEK composites has been, and is still being, well researched (Lustiger et al., 1990; Ngo and Ishida, 1987). Ultrapak or PEKEKK is a newer derivative of PEEK, developed partially to surpass PEEK in properties, as well as for commercial competitive reasons (Beland, 1991). The Ultrapak freeform composite was processed in a different manner from traditional compression molding. The optimum processing parameters are still being defined.

2.3.9. Summary: MFBs of 30% chopped fiber reinforced PEEK have been evaluated for use in flexural testing. Despite the small dimensions of the miniflexbars, 1 x 5 x 30 mm, a size effect was not evident. This was determined by closely examining microstructure and relating the microstructure to flexural behavior. The small size of the minibars also enabled the characterization of the flexural properties throughout the bar. The impact of the release of residual stresses upon cutting the minibars is not completely understood. Although residual stresses were shown to be present, they were small.
2.4. Discussion

The fiber orientation observed in the injection-molded 30% CFRPPEEK bendbar exhibited a skin core structure similarly found for many injection-molded composites (Nimmer and Trantina, 1985; Folkes, 1982; Freidrich, 1991). However, the location of the gate on the upper side of the bendbar rather than the top of the bendbar resulted in a skin of aligned fibers that was thicker on one side than the other. In addition, nonhomogeneity of fiber orientation in the core region was observed. Fiber orientation ranged from being entirely transverse, to being almost fully aligned. Attempts have been made to model an injection-molded bar as three layers, two skins and one core, to account for the influence of the variation in fiber orientation (Nimmer and Trantina, 1985). It is apparent from the microstructure of the CFRPPEEK bendbar that this type of modelling may account for some of the influence of fiber orientation; much information, however, is still lost.

The analysis of flexural properties of MFBs of chopped fiber reinforced PEEK has focused on fiber orientation as the predominant factor determining flexural properties within a well processed composite. However, since PEEK is a semicrystalline polymer, a question exists about the influence of matrix crystallinity on composite flexural properties. Before this can be answered, examination of the effect of processing conditions on matrix crystallinity should be examined.

For an unreinforced semicrystalline polymer, such as PEEK,
injection molding can cause a skin-core effect with respect to the degree and form of matrix crystallinity (Hsiung et al., 1990; Ballara et al., 1986). The effect of processing conditions on the morphology of PEEK composites has also been shown to be extensive (Tung and Dynes, 1987; Lee et al., 1986). Spherulitic growth of PEEK is nucleated both from within the matrix and at the fiber surfaces. A characteristic of PEEK that results in good matrix adhesion between carbon fibers and PEEK is the nucleation of PEEK on the fibers (Seferis, 1986, Lee et al., 1986). Interestingly, it was found that within an injection-molded composite PEEK specimen, the heterogeneity of crystallinity was less than within an unfilled PEEK specimen (Ballara et al., 1986). This was thought to be due to the high thermal conductivity of the carbon which can result in a more homogeneous spatial distribution of cooling rates.

The crux of all of this is that processing conditions can effect crystallinity of the matrix. And, just like fiber orientation, crystallinity will vary within the composite. However, the influence of crystallinity on mechanical properties of composites is still under debate. It has been recognized that crystallinity content will influence fiber/matrix adhesion (Saiello et al., 1990), which will therefore influence mechanical properties. However, if the degree of crystallinity is such that good fiber matrix adhesion is achieved, how will it further influence mechanical properties? In a study examining modulus and fracture toughness of chopped fiber PEEK composites under various processing conditions, it was concluded...
that the nature and orientation of the fibers was most important, and
crystallinity (for their range of processing conditions) was not
significant (Freidrich et al., 1991). Other researchers have also
concluded that PEEK composite fracture is not significantly
influenced by crystallinity, being overpowered by fiber effects
(Crick et al., 1987; Barlow et al., 1990; Mishra and Schultz, 1991).

Further evidence for the greater influence of fiber orientation
on mechanical properties compared to differences in matrix
crystallinity is provided by models predicting mechanical properties
based on fiber orientation. Good agreement has been shown between
experimentally determined mechanical properties and predicted
mechanical properties based primarily on fiber orientation (Bozarth
et al., 1987). The results of flexural testing the CFRPEEK MFBs have
also indicated a strong correlation between fiber orientation and
flexural properties. Although crystallinity could have been
determined for each MFB, it would probably have been overshadowed by
fiber orientation effects.

Another issue to be considered is the shapes of the
stress/strain curves that were observed from flexural testing the
CFRPEEK MFBs. Some of the curves were typical of final catastrophic
failure (Figure 2.10a). Others exhibited a stepwise failure (Figure
2.10b). This suggests two different modes of failure. Several
reports have described the modes of crack propagation through chopped
fiber reinforced composites under flexural loading conditions. The
primary means of crack growth has been observed to be fiber avoidance
(Shirrell, 1985). Whether the matrix material is ductile or brittle, and the fibers glass or carbon, the crack grows around fibers on a local scale, avoiding any clumps of fibers. Because of the fiber avoidance mode of crack growth, the fracture surface may be zig zagged on the surface and through the thickness (Mandell et al., 1982, Shirrell, 1985). Since the mechanical properties of a specimen under three point flexural loading are sensitive to the nature of any microstructural variation near the tensile surface of the specimen, a tortuous crack path on the tensile surface is expected to be followed to avoid fiber fracture. This was seen to occur with the CFRPEEK MFBs. Scanning electron micrographs revealed few fibers that were broken, rather many fiber ends were seen. Because of the fiber avoidance mode of fracture, and the transitions in fiber orientation seen in individual MFBs it is possible that the stepwise fracture tail in the stress/strain curves was due to fiber orientation.

Examination of the CFRPEEK MFBs under SEM also revealed several apparently contradictory details. Fibers both well coated with matrix and uncoated were found within the same MFB. This has also been observed in a study examining 30% CFRPEEK compact tension specimens for fatigue crack propagation (Freidrich et al., 1986). In these compact tension specimens, fracture was dominated by fiber/matrix separation along the interfaces of fibers oriented parallel to the crack direction and by rupture of the polymer material between them. In regions where fibers were oriented perpendicular to the crack front, no fiber pull-out was found,
instead, the crack followed a path of fiber avoidance.

Another difficult observation was the transition in several MFBs in the appearance of the fracture surface on the tensile side compared to the compressive side. This was marked by a change of the matrix appearing highly ductile to appearing brittle. Although confusing, this phenomenon of a highly ductile matrix coupled with a brittle matrix has been reported previously for PEEK composites.

Mandell et al. (1982) observed ductility through the thickness of fracture toughness specimens of 30% CFRPEEK. He postulated that the ductility was in response to shear stresses resulting from relative movement of adjacent groups of fibers, rather than plane stress effects at the surface. This observation with standard size specimens is especially important, since increased ductility could mean that the state of stress for the MFBs is plane stress rather than the desired plane strain.

An increased amount of ductility was also observed at the fracture surfaces of the MFBs compared to the standard size specimens (Mason et al., 1991). Ductility of the polymer matrix has been attributed to be a function of the loading conditions applied (Freidrich et al., 1986). A much greater amount of matrix deformation was observed if the fracture was induced under static loading conditions. In slow fracture, the ductile thermoplastic matrix may be easily detached from the fiber surfaces and deformed (another reason why bare fibers may be seen). Crack propagation (ductile fracture) is thus believed to be the dominant failure energy
absorption process for a slow fracture, while it is crack initiation (brittle failure) that is prevalent for fast fracture, which is dominated by the fibers and fiber-matrix interface (Wu and Schultz, 1990).

The CFRPEEK MFB fracture surfaces can be examined in light of the above observations. First, the slower crosshead rate of the MFBs (0.5 mm/min) compared to the rate used with standard MFBs (1.7 mm/min) may account for the increased ductility observed between the MFBs as compared to the standard size bars. However, it should be noted that the strain rate of 0.01 min⁻¹ remained the same between both the MFBs and the standard size specimens. Another possibility is that the cracking began slowly, but eventually speeded up once it began propagating. This may account for the occurrence of ductile morphology (slow crack) and brittle morphology (fast crack) from the tension to the compression side of the specimen.

Further evidence for a ductile/brittle phenomena based on the speed of fracture has been given in the literature for APC-2 (continuous fiber reinforced PEEK). APC-2 specimens subjected to double cantilever tests were characterized and the features observed were related to the fracture modes (Barlow et al., 1990). Two rates of crack growth, fast and slow were observed. Generally slow crack growth preceded fast crack growth. Different morphologies were associated with each. The resin fracture surface showed much more ductility in the slow region, with long tufts of resin drawn out from anchor points on the fiber surface. In the fast crack region, the
resin covering the fibers displayed a fine microductility often forming a rosette pattern. The authors state that both types of fracture surfaces are indicative of good fiber matrix adhesions. At slow deformation rates or high temperatures, the polymer is able to deform and draw out. When this is not possible, only very localized plastic deformation can occur, giving the fine scale markings. The rate at which the fracture surface changes from that characteristic of slow to that of fast crack propagation rate is influenced by the temperature. For the fast propagation rates, fibers covered with microductile resin are observed regardless of whether the matrix is crystalline or anorphous, although the pattern of microductility appears to be influenced by the spherulitic texture of the matrix. At the slower rate, the matrix had time to deform and draw out from its attachments on the fiber, and the stress distribution encouraged strain in the vicinity of the fiber/matrix interface. The tougher the matrix, the closer the final failure was to the fiber surface.

In another study the fracture surface of APC-2, obtained by splitting the samples under the wedging action of a blade driven into the material, was examined (Crick et al., 1987). These surfaces were considered representative of cracks propagating parallel to the fibers and normal to the prepreg layers. Similar to the previous study the authors observed stable (slow) and unstable (fast) fracture. Approximately 36% of the fracture area was stable failure. SEM showed that the level of plastic deformation was higher in the stable growth regions. Regions of plastically deformed material
radiating from central points in the form of rosette patterns were related closely to the spherulitic texture of the PEEK. There was extensive fiber damage in both regions.

Propagation of an interlaminar crack through the polymer has also been described (Crick et al., 1987). An important feature that was observed was the presence of zones of deformed polymer which extended into the bulk of the material from the fracture surface. These zones were representative of permanent deformation of the polymer and therefore a contribution to the energy absorbed in interlaminar fracture.

From these studies it is apparent that the appearance of matrix ductility is a positive phenomenon. If the APC-2 composite was not well processed, for instance, and had reduced fiber/matrix adhesion, the fracture surface would indicate fibers with very little resin on them (Barlow et al., 1990). The resin would also show little ductility even during slow fracture. The matrix would be torn without drawing out to any extent, because the crack would propagate along the fiber/matrix interface before the ductility of the matrix can be realized. This low matrix ductility is a consequence of poor load transference between fibers and matrix. At a fast crack rate, the resin ductility would be even further reduced, and the fibers again would have very little matrix adhering to them (Barlow et al., 1990). Therefore, a prerequisite to the development of a deformation zone is that the interface between the fiber and the matrix must be good in order to ensure that the stresses are
transferred back into the bulk of the composite (Crick et al., 1987).

These observations, although made about APC-2, may explain why
a transition region from ductile to brittle morphology was observed
in the CFRPEEK MFBs. This now appears to have been possibly a
transition from slow fracture to fast fracture. Although an attempt
was made initially to find a correlation between decreasing flexural
strength and degree of matrix ductility, one could not be found.
Considering the previous explanations, it is apparent that a high
degree of matrix ductility is not necessarily a liability in flexural
strength.

One of the purposes for studying injection-molded composites
was the anticipation that these composites could be easily produced
in a variety of sizes to fit patients (Gillett et al., 1984; Mason et
al., 1992). A problem that will be encountered in realizing this
goal is characterization difficulties, specifically fiber orientation
effects. For every shape and size difference, the thickness of the
edge and core regions will change, along with subtler differences in
fiber orientation and distribution (Folkes, 1982). Adding holes or
other increasingly complex design features, will enhance the
difficulty of characterization. Using MFBs to characterize a
potential composite material for orthopaedic applications was shown
to be successful. However using these MFBs to evaluate each possible
composite implant design would be cumbersome. The use of injection-
molded composites in implants may be limited by the difficulty that
is encountered in order to characterized them.
3. Exposure

3.1. Introduction: The use of polymer composites in orthopaedic applications requires an evaluation of the long-term mechanical properties after exposure to an in vivo environment. This has been accomplished in the past by bench testing standard size test specimens that have been exposed in vitro to various environments for various time periods, by testing retrieved implants that have been implanted in large animals, and by testing retrieved clinical implants. For all of these methods, gathering of long term data requires the exposure or implantation of the composite for several years or more. Problems with mechanically testing retrieved implants include the testing of complex geometries making comparison of data between composite material and device difficult. The use of MFBs can overcome both of these problems. The decreased depth, and thus an increased surface area to volume ratio, as compared with standard size bars, can result in observing effects of the environment on the bulk properties of the composite in a shorter period of time than for a larger volume of material. Also, miniflexbars implanted in vivo can be tested in flexion after removal, resulting in mechanical data which can be compared to other materials tested in flexion.

Many of the results of the multiple studies evaluating the effects of a fluid environment on CFRPEEK and CFRPSU are short-term (365 days or less) (Brown et al., 1990; Kwarteng and Stark, 1987). For orthopaedic applications, composite materials will be expected to exist in a changing stress environment, essentially non-degraded, for
a human's lifetime. Being able to predict a material's long-term in vivo performance based on in vitro testing, or short-term in vivo testing, can be very valuable. Several tests use elevated temperatures to accelerate the degradation process of short-term testing (Agarwal and Broutman, 1980; Wagner 1989). There is a possibility that accelerated temperature can also be used for modulus prediction based on the principle of time-temperature superposition. Because of the viscoelastic nature of polymers, master curves can be obtained for polymers that predict the behavior of the polymer at long times, by using elevated temperatures at short time periods (Aklonis and MacKnight, 1983). This principle was successfully applied to amorphous polymers, although it is only quantitatively correct for limited time-temperature ranges (Aklonis and MacKnight, 1983). In addition it cannot be applied to multiphase or semicrystalline polymers (Aklonis and MacKnight, 1983), and most likely not to composites. Using elevated temperatures in addition to exposure for evaluating the response of composites may be a more vigorous test, however, prediction of long-term properties is limited.

The possibility of predicting the behavior of polymer composites exposed to moisture at extended time periods by using data generated from short-term studies has also been attempted by other means. One procedure has focussed on determining the test conditions required to achieve a desired moisture content in the shortest time (Cirascili et al., 1987). This was accomplished by increasing the
relative humidity for a period of time to accelerate the effect of the humidity and then decreasing the relative humidity to a level that would allow the desired moisture content in the composite to be achieved. This method is not feasible for composites intended for in vivo applications since the in vivo environment is at a constant temperature and at 100% relative humidity.

Exposure of polymer composites to fluid environments can alter short-term and long-term stability of mechanical properties. The degradation of composite materials may result from several factors including the loss of strength of the reinforcing fibers by stress corrosion, the loss of adhesion and interfacial bond strength from degradation of the fiber-matrix interface, chemical degradation of the matrix material, dependence of the matrix modulus and strength on time and temperature, and accelerated degradation caused by combined action of temperature and chemical environment (Agarwal and Broutman, 1980). The degradation of the matrix material results in severe deterioration of all composite properties, whether they are fiber-dominated or matrix-dominated. In the case of matrix-dominated properties, such as the properties of unidirectional composites in the transverse direction and properties of short-fiber composites, even a small variation in the matrix properties will be reflected in composite properties (Agarwal and Broutman, 1980).

Moisture absorption in the composite is mostly by matrix diffusion. It can also take place through the cracks and voids at the fiber matrix interface. These effects have been very evident in both
glass-fiber, carbon-fiber-reinforced epoxies, and thermoplastics such as polycarbonate, (Robeson et al., 1986). The high performance thermoplastics in composites now being considered for use in orthopaedic implants, such as PSU and PEEK, generally have better chemical and heat resistance than the earlier thermoplastics. PSU is an amorphous polymer. PEEK is a semicrystalline polymer. In general semicrystalline polymers are more solvent resistant than amorphous polymers due to the densely packed spherulites in the crystalline region which impedes diffusion of solvents into the polymer (Beland, 1990).

Many tests have been carried out to evaluate PEEK and PEEK composites in a variety of environments. Since PEEK and its composites have been developed primarily for use in the aviation industry, studies examining the effects of PEEK in contact with a number of fluids typically encountered in aviation applications have been completed. PEEK and its carbon composites have been shown to generally be resistant to Skdrol, an aviation hydraulic fluid, (Cogswell and Hopprich, 1983; Stober et al., 1984), ethanol, Freon and trichloroethylene (Whitaker et al., 1986). Methylene chloride was rapidly absorbed, with the degree of sorption dependent on crystallinity (Stober et al., 1984).

Although the excellent resistance to many aggressive chemical environments are reassuring for the potential application of PEEK in orthopaedics, studies examining the effects of exposure to water are more pertinent. The earlier studies were done with Aromatic Polymer
Composite -1 (APC-1, consisting of Hercules AS4 3K fiber tows in PEEK Matrix) the predecessor to APC-2, the continuous fiber PEEK composite that is now being marketed. Although APC-1 was not considered to be as good as APC-2 (and hence the change), there was no detectable effect on flexural properties of APC-1 after 24 hours in boiling water (Cogswell and Hopprich, 1983). However, after 33 days in 80°C water, the tensile strength of neat PEEK decreased by 5% (Cogswell and Hopprich, 1983). In another study the effects of exposure of neat PEEK films of varying crystallinities for approximately 12 days, to water, and methylene chloride was determined. Sorption of water in the PEEK films was minimal, .1%, although it increased with increasing temperature. The effect of crystallinity was not noted for the water sorption studies, as it was likely the polymer absorbed a small amount of water.

Exposure of neat PEEK and APC-2 to humid air has also been examined (Wang and Springer, 1989) to determine the effects of varied moisture content and crystallinity on the fracture toughness. Tests were conducted with neat PEEK 150P specimens having 30,34, and 43 % crystallinity and with APC-2 specimens having 17 and 21 % crystallinity. One inch square specimens were exposed for 15 days to relative humidities ranging from 60-100 % and temperatures ranging from 140-200°F. The fracture toughness was found to be unaffected by crystallinity and by moisture content. Moisture absorption by both PEEK 150 and APC-2 followed the classical, class I Fickian diffusion. The maximum moisture contents and the diffusivities were described by
expressions similar to those developed for epoxy matrix composites.

A different study examined the sorption of neat PEEK specimens, 2 mm thick, immersed in water at elevated temperatures (Grayson and Wolf, 1987). The solubility of water increased from 0.44% at 35°C to 0.55% at 95°C. The diffusion coefficients for sorption, desorption and resorption were found to be equal. The author postulated that the morphology of the matrix does not change during water sorption and/or desorption. Also, the morphology did not change during prolonged immersion (saturation) in water at 95°C.

In general, polysulfone exhibits excellent resistance to aqueous, mineral acid, alkali, and salt solutions. Its resistance to detergents and hydrocarbon is good even at elevated temperatures under moderate levels of stress (Rubin, 1990). In polar organic solvents such as ketones, chlorinated hydrocarbons and aromatic hydrocarbons, polysulfone will swell, dissolve or stress crack (Beland, 1990). It is also attacked under stress by low molecular weight solvents (Rubin, 1990). The sorption of water in neat PSU varies from 0.6% to 1.1% depending on the grade of PSU (Beland, 1990).

Several studies have evaluated PEEK and PSU specifically for use in vivo. Short-term degradation effects of chopped CFRPEEK exposed to saline showed no significant difference in the flexural properties of specimens 6.4 x 12.5 x 125 mm after 3 weeks (Brown et al., 1990). In contrast, the flexural strength of 30% CFRPSU specimens (of the same dimensions) was significantly decreased by
saline soaking (Brown et al., 1990). However, saline aging of 30% CFRPSU fracture toughness test specimens did not cause significant changes. No reduction in transverse flexural strength for APC-2 was found after 340 days in boiling saline solution, although an uptake of 0.3% moisture was observed (Kwarteng and Star, 1990).

In another study, characterization of environmental effects were performed on APC-2 and CFRPSU laminates that would be used in composite hip prostheses (Maharaj et al., 1991). Specimens for flexural testing were 127 mm x 3.15 mm x 25.4 mm. Reductions in flexural and compressive strength of 40% were observed for CFRPSU after immersion at 37°C and 90°C for 1.5 years. APC-2 exhibited a 10% reduction in compressive strength but no statistically significant reduction in flexural strength after immersion at 37°C for 1.8 years. Immersion at 90°C for 1.5 years resulted in a 16% reduction in both the flexural and compressive strength of APC-2. It was noted that moisture absorption in PEEK is highly sensitive to temperature. However, percent increase in absorption with time at constant temperature was observed not to be linear. The percent absorption equilibrated after 110 days at 37°C and at 90°C, plateaued at 120 days, but then rose again at 200 days and kept on increasing. A Moisture content of 0.35-0.36% was measured after immersion for 340 days at 90°C. However at 541 days the moisture content was 0.43% and had not plateaued. The authors suggest that the reduction in flexural strength observed for the APC-2 specimens immersed at 90°C may have occurred near the end of the immersion period due to the
same long term environmental degradation mechanism which caused the moisture content to increase again after initially remaining stable.

The moisture absorption data of the APC-2 hip stems exhibited a significant scatter attributed to moisture trapped between the ceramic head and the trunions. After 531 days of immersion the moisture content of the stems varied between 0.3-0.48%. The stems also exhibited a 14% decrease in static strength following immersion at 90°C. The authors also concluded that CFRPSU composites undergo significant environmental degradation following long-term exposure to simulated in vivo environments.

The effects of steam sterilization on polysulfone, polycarbonate, polyestercarbonate, polyethersulfone and polyetherimide were evaluated (Robeson et al., 1986). They found hydrolytic stability of polysulfone under severe conditions. The tensile strength of the PS remained the same although the impact strength decreased with increased number of times of autoclaving. In other work, composite PSU hip stems immersed in 0.9% saline solution maintained at 90°C for one week lost 10% of their original strength (St. John, 1983).

Examination of the mechanical properties of CFRPSU or CFRPEEK exposed to physiological fluid (blood, plasma, or serum) has been limited. Ultimate bond strengths of carbon fiber PSU measured using a single fiber-microdroplet pull-out test indicated that dry bond strengths were significantly decreased following exposure to either saline or an inflammatory exudate from rabbits, (Latour and Black,
1992). CFRPSU laminates made into fracture fixation plates were tested for flexural properties after 16 weeks and 12 months implantation on canine femora (McKenna et al., 1980). At 16 weeks it was concluded that there was no systematic change in stiffness or strength of the plates after removal. However, after 12 months, a definite effect of implantation on the CFRPSU plates was noted. Two plates warped and lost stiffness, while another plate lost strength. The ability of CFRPEEK was found to be better than that of CFRPSU in resisting environmental stress cracking in simulated physiological environments including lipid solutions and human blood (Davidson et al., 1991). Further investigation of the effects of the physiological environment on PEEK is necessary.

The objective of the present study was to expose the CFRPEEK MFBs, that have previously been characterized, continuous fiber MFBs and CFRPSU MFBs to serum for an extended time period. The results of this study will be used to evaluate the materials' flexural properties after exposure, as well as to examine the feasibility of using MFBs for accelerated environmental testing as compared to using standard size specimens.
3.2. Materials and Methods

3.2.1. Materials: The materials tested in this study included injection molded 30% chopped-carbon-fiber-reinforced polyetheretherketone (CFRPEEK) injection molded bendbars (450CA30-pellets received from ICI Chemicals and processed at Dexter composites, Cleveland Ohio). These bendbars were from the same batch of bendbars that were tested for standard size flexural properties (Mason et al., 1992). Compression molded 61% continuous fiber reinforced PEEK, 8 ply unidirectional laminate (APC-2 plies (ICI Chemicals) processed at Smith and Nephew Richards, Memphis Tennessee) were also examined. Lastly, injection molded 30% chopped carbon fiber reinforced polysulfone (CFRPSU) (PS-30PANC, LNP Corp., Malvern Pennsylvania) was used. This CFRPSU material had previously been sterilized twice in an autoclave using 90 KPa, 121°C, for 20 min (Brown et al., 1990).

Miniature flexural bendbars (MFBs) were cut from each of the above materials using a slow speed saw with a diamond wafering blade (Buehler). The 30% CFRPEEK MFBs were cut as indicated in Figure 2.3. The test MFBs comprised a set of Y MFBs (9 MFBs from each of sections A, B, C and D) and a set of Z MFBs (8 MFBs from each of sections A, B, C and D). The control MFBs consisted of a set of Y MFBs from section B, and a set of Z MFBs from section B. The dimensions of the Y and Z MFBs were approximately 1 x 6 x 30 mm.

The laminate CFRPEEK was sanded with 240 grit carburundum paper to remove the surface finish. Transverse MFBs and longitudinal MFBs
were cut from the laminate as indicated in Figure 3.1. Both the test and control specimens included ten longitudinal and ten transverse MFBs.

CFRPSU MFBs were cut as indicated in Figure 3.2. As seen in the diagram, the IM bars had been previously tested in three-point bend, with the fractured halves reserved for fracture toughness testing (Brown et al., 1990). MFBs were cut from the fractured halves of the fracture toughness specimens (the halves representing 1/4 of the original injection molded bendbars). The test specimens were cut as Y MFBs from sections A and B of IM bar # 1 and the control specimens were cut as Y MFBs from sections A and B of IM bar # 2. Apparent in Figure 3.2 is that in the original injection molded bars, the gate is located in the center at the end of the bar. This is in contrast with the side location of the gate at the end of the CFRPEEK IM Bars (Figure 2.3). Therefore, the fiber orientation and distribution of the CFRPEEK MFBs cannot be considered as equivalent to the fiber orientation and distribution of the CFRPSU MFBs (although cut in similar positions from the IM bendbars).

The edges of the cut MFBs of all materials were lightly sanded to remove any burrs or irregularities. The edge MFBs cut from the I-M CFRPEEK and CFRPSU bars (#1 and #9 of the Y MFBs and #1, #4, #5, and #8 of the Z MFBs) were sanded on the cut surface (with 240 grit carburundum paper) to achieve a uniform thickness.
Figure 3.1. Sectioning of unidirectional APC-2 composite into 1.5 mm thick longitudinal and transverse MFBs.
Sectioning of IM 30% CFRPS bendbar (6.4 x 12 x 120 mm)

i. The CFRPS bendbar was previously tested in three-point-bend

ii. The fractured halves were then used in fracture toughness testing

iii. The sections remaining after fracture toughness testing were cut into Y MFBs

Figure 3.2. Sectioning of 30% CFRPSU into MFBs.
3.2.2. Change in Weight: Once cut, each MFB was ultrasonically cleaned with distilled water and detergent for 5 minutes. The samples were then rinsed with distilled water and placed back into the ultrasonic cleaner for another 5 minutes. The samples were removed and placed in an aluminum foil tray to be dried in a 50°C oven (Blue M stab therm gravity oven) for 24 hours. Once dried, the samples were placed into polystyrene tubes and put under moderate vacuum (app. 460 mm Hg) for one hour, after which they were weighed on an electronic microbalance (Mettler AE 163) to 5 digits. Samples were weighed three times, and the average value was used as the dry sample weight. At the end of the soaking time period, the test samples were mechanically tested and the fractured halves were blotted dry with a tissue (Kimwipe) and weighed. To assure that weighing after mechanically testing did not distort the postweight values, the control samples were weighed both before and after mechanical testing. All samples were weighed in triplicate, and the average value was used as the postweight. The percent change in weight due to soaking was determined by

\[
\% \text{ change} = \frac{(\text{preweight} - \text{postweight}) \times 100}{\text{preweight}}
\]

3.2.3. Exposure to In Vitro Environment: Once samples were washed, dried and weighed as described above, they were ready for exposure in a simulated physiologic environment. A solution of 10% (by volume) calf serum, 10% penicillin streptomycin (penicillin: 50,000 units/100 ml, streptomycin: 50 mg/100 ml), and 80% sterile saline
was prepared. If frozen, the solution was thawed in a 37°C water bath for 2-3 hours. If freshly made, the solution was brought to 37°C in a water bath before use. The following protocol was followed for the initial exposure of the samples to the serum solution. The equipment that was needed included plastic disposable 5 ml pipettes, pipette holder and bulb, forceps which could be flamed, polystyrene tubes (Falcon 2054, 12 x 75 mm round bottom tube with cap) for samples, prelabelled in a Styrofoam holder, 100% ethanol (not denatured) to flame forceps, sterile saline in sterile tube, samples in tubes without caps, 70% ethanol, Bunsen burner and a hair cap. The working area was first cleaned and disinfected with a detergent solution. The burner was lit and adjusted for a blue flame. Each time forceps were used to pick up the sample they were flamed. Samples were removed with forceps from their tubes, and rinsed with 70% ethanol for approximately 30 seconds in order to sterilize them. Each sample was then rinsed in saline and placed in a new tube. This was repeated until all samples had been placed in new tubes. 2.5 ml serum was then pipetted into each tube. Samples were capped and put into an incubator at 37°C.

Every two weeks the serum was changed. If there were any signs of infection (the serum was turning cloudy), the samples were transferred into new tubes following the procedure above. If the serum was clear, the old serum was pipetted out and new serum pipetted in without changing tubes, but still following aseptic technique which included resterilizing the specimen.
3.2.4. Modulus Testing - 30% CFRPEEK: Since each MFB has a
different microstructure as a result of varying fiber orientation and
distribution, it was desired to have each MFB serve as its own self-
control. The hope was to test each MFB in 3-point-bending at
designated time periods, only for modulus, until the end of the
soaking period, at which time the MFBs would be tested to failure.
To determine if this was feasible, the results of the three-point-
bend testing of a previous set of Y and Z MFBs were used. A
correlation was found between ultimate flexural strength and flexural
modulus for both the Y MFBs (Figure 3.3a), and the Z MFBs (Figure
3.3b). The $R^2$ value for the correlation between strength and modulus
for the Y MFBs (calculated from simple linear regression) was 0.9,
and for the Z MFBs was 0.84. Therefore, it was thought possible to
use modulus testing as a method of self-control. To do this, the
maximum elastic load for each sample from the previous set of Y and Z
CFRPEEK MFBs was determined as shown in Figure 3.4. The point where
the load-displacement curve deviated from linearity was considered a
conservative estimate (as compared to the 5% secant line) of the
maximum allowable load before plastic deformation would occur. This
determination of where the elastic region ended and the plastic
region began was the same as that used in the characterization
section.

Maximum elastic load vs. depth of the MFB is plotted in Figure
3.5(a,b). From these graphs, a minimum elastic load limit of 21.77 N
is observed for the Y MFBs (for MFBs with a depth greater than 0.8
Figure 3.3a. Correlation between flexural strength and modulus for the Y CFRPEEK MFBS.
Figure 3.3b. Correlation between flexural strength and modulus for the Z CFRPEEK MFBs.
Figure 3.4. Determination of maximum elastic load. The point where the line tangent to the load-deflection curve deviates from the curve was considered to be the elastic load limit.
Figure 3.5a. Elastic load limit versus depth for the Y MFBs.
Figure 3.5b. Elastic load limit versus depth for the 2 MFBs.
mm), and a minimum elastic load limit of 18.40 N is observed for the Z MFBs. A load of 17 N was considered to be the maximum allowable load for the modulus testing.

To assure that the modulus could be tested repeatedly without an associated loss in stiffness, three trial Y MFBs were first tested without any exposure to serum. As shown in Figure 3.6, the modulus of these MFBs did not decrease after 13 or 15 tests.

Although the loads applied to test the modulus were well below the onset of plastic deformation, to insure that permanent damage was not being caused by modulus testing an additional set of controls were prepared. A set of BZ MFBs and BY MFBs were cut to serve as controls. These MFBs were not exposed to serum, however they were modulus tested at the same times that the exposed MFBs were.

Y and Z CFRPEEK MFBs were to be tested after 24 hours of serum exposure, 1 week, 2 weeks, and then every 2 weeks until removal. The protocol described above for the initial placement of the MFBs in the serum solution was followed after testing at each time period. Note that only the 30% CFRPEEK MFBs were modulus tested prior to being tested to failure.

3.2.5. Flexural Testing: At the end of the designated time period, the MFBs (30% CFRPEEK, PEEK laminate and 30% CFRPSU) were tested in three-point-bending as described previously for the characterization of the CFRPEEK MFBs. For the PEEK laminate MFBs, different supports and loading nose were used in order to increase the support span from
Preliminary Modulus Testing

Figure 3.6. Preliminary modulus testing for three BY MFBs.
16.07 mm to 24 mm. This was necessary since the thickness of the laminate MFBs was approximately 1.5 mm, and a 16:1 span to depth ratio was required. The rate of loading also increased to 0.64 mm/min. All MFBs were tested directly from the tube, without first being wiped off. A thin coating of serum solution adhered to each MFB, thus allowing the MFBs to be tested while exposed to the in vitro environment.

3.2.6. Enhanced Degradation: Since effects of exposure on the flexural properties of CFRPEEK MFBs was expected to be minimal, an experiment was designed to enhance the possible degradation. Hose clamps were modified into miniature three-point-bending fixtures as shown in Figure 3.7. Rods of polyethylene were used as the supports and loading nose. A CFRPEEK MFB was placed between the three rods, and the hose clamp screw was tightened until appreciable deformation could be observed (but before the MFB broke). Eight MFBs were tightened into 8 hose clamps, placed into beakers of 10% serum and incubated at 37°C for 18 weeks. Since the MFBs were strained well past the elastic limit, the bars could not be tested in flexure after removal from the serum. However, the fracture surfaces of these bars could be examined with SEM and compared to the surfaces of the unstressed but exposed CFRPEEK MFBs.
Figure 3.7. Enhanced degradation experimental set-up for 30% CFRPEEK MFBs.
3.3 Results

3.3.1 18 weeks exposure - 30% CFRPEEK: The original idea to test the modulus of the CFRPEEK MFBs every two weeks until the end of the study was modified after examining the first two weeks of modulus data. Shown in Figure 3.8., the moduli of the exposed Y MFBs and the control BY MFBs did not change during the four test periods. The same was true for the exposed Z MFBs and the control BZ MFBs for the first two test periods. Since a change in modulus was not being observed, it was deemed that the exposed MFBs would not have to be monitored that closely. A decision was made to wait until 18 weeks, the halfway point in the experiment, to test two groups of MFBs to failure. If a change in flexural properties was observed, then modulus testing could continue, if not, then the rest of the MFBs would be tested to failure at 36 weeks without intermittent modulus testing.

At 18 weeks, the exposed BZ MFBs, the modulus control BZ MFBs and the Exposed AY MFBs were tested to failure. Comparison of modulus at failure for the exposed BZ MFBs with the pretest modulus indicated a significant decrease (Table 3.1). However, a decrease was also observed for the modulus-control BZ MFBs. Also shown in Table 3.1 is that the average pretest modulus values for both the exposed MFBs and the modulus-control BZ MFBs are higher than the average modulus calculated for the original BZ MFBs tested in the characterization experiments. A difference was not observed when comparing the modulus-control MFBs with the original MFBs for the modulus
Figure 3.8. Modulus testing of the CFRPEEK MFBs up to 24 hours (Z MFBs) or 2 weeks (Y MFBs).
Table 3.1. Results from modulus testing BZ and BY CFRPEEK MFBs. Original indicates MFBs that were tested in the characterization section. These MFBs were not modulus tested or exposed. Control indicates MFBs that were modulus tested but not exposed.

<table>
<thead>
<tr>
<th></th>
<th>Pretest Modulus (GPa)</th>
<th>Modulus @ failure (GPa)</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZ-18wks</td>
<td>15.90 (2.91)</td>
<td>12.55 (2.53)</td>
<td>27.1 (4.7)</td>
</tr>
<tr>
<td>BZ-18-control</td>
<td>15.56 (3.78)</td>
<td>14.05 (3.24)</td>
<td>10.5 (8.1)</td>
</tr>
<tr>
<td>BZ-original</td>
<td></td>
<td>14.56 (2.82)</td>
<td></td>
</tr>
<tr>
<td>BY-36wks</td>
<td>17.10 (2.40)</td>
<td>15.55 (2.07)</td>
<td>10.2 (6.3)</td>
</tr>
<tr>
<td>BY-36-control</td>
<td>16.56 (2.07)</td>
<td>15.57 (2.59)</td>
<td>7.8 (12.8)</td>
</tr>
<tr>
<td>BY-original</td>
<td></td>
<td>15.66 (1.94)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2. Flexural test results for AY and BZ 30% CFRPEEK MFBs after 18 weeks exposure to 10% serum. Original indicates MFBs that were tested in the characterization section. These MFBs were not modulus tested or exposed. Control indicates MFBs that were modulus tested but were not exposed.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Mod.(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AY-Control</td>
<td>9</td>
<td>266.6(42.4)</td>
<td>3.86(.53)</td>
<td>11.8(4.0)</td>
</tr>
<tr>
<td>AY-18wks</td>
<td>9</td>
<td>245.0(53.0)</td>
<td>4.00(.85)</td>
<td>9.3(2.5)</td>
</tr>
<tr>
<td>BZ Original</td>
<td>8</td>
<td>283.9(41.2)</td>
<td>2.88(.29)</td>
<td>14.6(2.8)</td>
</tr>
<tr>
<td>BZ Mod-cont</td>
<td>8</td>
<td>285.4(54.1)</td>
<td>2.87(.23)</td>
<td>14.0(3.2)</td>
</tr>
<tr>
<td>BZ-Control</td>
<td>16</td>
<td>284.7(48.5)</td>
<td>2.88(.26)</td>
<td>14.3(3.1)</td>
</tr>
<tr>
<td>BZ-18wks</td>
<td>8</td>
<td>275.1(49.6)</td>
<td>2.72(.20)</td>
<td>12.6(2.7)</td>
</tr>
</tbody>
</table>
calculated when the MFBs were tested to failure. These results were also observed for the BY MFBs tested after 36 weeks exposure. Since it was shown that the modulus calculated in the pretest experiments gave artificially high values, the MFBs tested in the characterization experiments were used as controls, rather than the self-control pretest moduli. This is valid since, as shown in Table 3.2, a significant difference between the flexural results of the BZ modulus-control compared to the original BZ MFBs tested in the characterization experiment was not observed.

In Figure 3.9 stress, strain, and modulus are indicated for the AY and BZ MFBs after 18 weeks exposure to 10% serum. A significant difference was not found for any of the flexural properties between the exposed bars and the control bars. Figures 3.10 and 3.11 graph stress, strain and modulus of the individual MFBs with respect to location in the intact CFRPEEK bendbar. It can be clearly seen that the trends observed in the characterization experiments with the unexposed MFBs (control MFBs) are also observed with the MFBs that were exposed to serum for 18 weeks.

Table 3.3 shows the results for samples exposed for 18 weeks in serum at 37°C. At 18 weeks, the percent weight increase of the CFRPEEK AY MFBs was 0.39% compared to 0.35% for the BZ MFBs. The weight increase for the control BZ MFBs was 0.05%. This change may have been caused by moisture pick-up from the air.

Examination of the fracture surfaces of the exposed MFBs with SEM showed no noticeable differences when compared to the fracture
Figure 3.9. Flexural test results for AY and BZ 30% CFRPEEK MFBs after 0 and 18 weeks exposure to 10% serum.
Figure 3.10. Flexural stress, strain and modulus for each individual AY MFB after 0 and 18 weeks exposure to 10% serum. The MFBs are plotted by position.
Figure 3.11. Flexural stress, strain and modulus for each individual BZ MFB after 0 and 18 weeks exposure to 10% serum. The MFBs are plotted by position. The control MFBs had been modulus tested, but not exposed. The original MFBs had not been modulus tested or exposed.
surfaces of the control SEMs as described in Chapter 2. Areas of a
good fiber-matrix interface were found at the tensile surface of the
exposed MFBs. Matrix ductility and uncoated fibers were also
observed at the tensile surface, however these effects were also seen
with the control bars. Since an alteration in flexural properties of
CFRPEEK MFBs was not observed after 18 weeks exposure, the remaining
MFBs were left in serum until 36 weeks.

3.3.2. 36 weeks - 30% CFRPEEK: At 36 weeks the average percent
weight gain of the CFRPEEK MFBs was 0.385 (Table 3.4).
Interestingly, a significant increase was found for weight gain of
A&D MFBs compared to B&C MFBs (Figure 3.12). Within the B&C MFBs a
significant increase was observed for weight gain of the core bars
compared to weight gain of the edge bars. Two possible explanations
for this phenomena can be offered. First, an increased number of
aligned fibers at the surface of the edge bars compared to the core
bars decreases the amount of matrix that can absorb fluid. This
suggests that fluid is being absorbed by the matrix rather than at
fiber matrix interfaces. Alternatively, a greater number of fiber
ends are exposed in the core sections compared to the edge sections.
If these fibers have a poor fiber/matrix interface, moisture may be
taken up at the fiber/matrix interface by capillary action.

As seen in Figure 3.13 (and Table 3.5), average flexural
properties did not change after 36 weeks exposure of CFRPEEK MFBs to
10% serum. Differences in flexural properties were not observed for
Table 3.3. Percent weight change for AY and B2 CFRPEEK MFBs after exposure to 10% serum for 18 weeks. Control MFBs were modulus tested but not exposed.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>% weight change</th>
</tr>
</thead>
<tbody>
<tr>
<td>AY</td>
<td>.9</td>
<td>0.38879 (0.03007)</td>
</tr>
<tr>
<td>B2</td>
<td>8</td>
<td>0.35163 (0.02720)</td>
</tr>
<tr>
<td>B2-control</td>
<td>8</td>
<td>0.04804 (0.01377)</td>
</tr>
</tbody>
</table>

Table 3.4. Percent weight change of 30% carbon fiber reinforced PEEK MFBs after 36 weeks exposure to 10% serum.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Avg. (Std.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>17</td>
<td>0.067 (0.022)</td>
</tr>
<tr>
<td>A&amp;D</td>
<td>33</td>
<td>0.399 (0.032)</td>
</tr>
<tr>
<td>B&amp;C</td>
<td>34</td>
<td>0.372 (0.045)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>Away</td>
<td>32</td>
<td>0.378 (0.049)</td>
</tr>
<tr>
<td>Near</td>
<td>34</td>
<td>0.395 (0.032)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>A&amp;D,Away</td>
<td>32</td>
<td>0.396 (0.040)</td>
</tr>
<tr>
<td>A&amp;D,Near</td>
<td>31</td>
<td>0.403 (0.024)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>Edge</td>
<td>16</td>
<td>.375 (.031)</td>
</tr>
<tr>
<td>Core</td>
<td>15</td>
<td>.391 (.031)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>B&amp;C,Edge</td>
<td>23</td>
<td>0.350 (0.054)</td>
</tr>
<tr>
<td>B&amp;C,Core</td>
<td>44</td>
<td>0.384 (0.035)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>.0163</td>
</tr>
</tbody>
</table>
Figure 3.12. Percent weight change of 30% CFRPEEK MBs after 36 weeks exposure to 10% serum.
Table 3.5. Flexural test results for 30% CFRPEEK Y and Z HFBs and the B&C HFBs after 36 weeks exposure to 10% serum. Control indicates those HFBs that were tested in the characterization section.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y%Z-Control</td>
<td>84</td>
<td>282.6 (38.5)</td>
<td>3.13 (.51)</td>
<td>13.8 (3.06)</td>
</tr>
<tr>
<td>Y%Z-36wks</td>
<td>48</td>
<td>286.8 (39.0)</td>
<td>3.02 (.43)</td>
<td>13.9 (3.0)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>B&amp;C-Control</td>
<td>51</td>
<td>292.8 (37.3)</td>
<td>2.83 (.24)</td>
<td>15.1 (2.7)</td>
</tr>
<tr>
<td>B&amp;C-36 wks</td>
<td>26</td>
<td>299.2 (39.4)</td>
<td>2.85 (.43)</td>
<td>15.1 (2.8)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>B&amp;C,Core -C</td>
<td>34</td>
<td>277.3 (32.9)</td>
<td>2.92 (.23)</td>
<td>14.0 (2.4)</td>
</tr>
<tr>
<td>B&amp;C,Core-36</td>
<td>18</td>
<td>285.2 (37.5)</td>
<td>2.84 (.25)</td>
<td>14.1 (2.7)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>B&amp;C,Edge -C</td>
<td>17</td>
<td>323.7 (24.2)</td>
<td>2.66 (.14)</td>
<td>17.3 (1.7)</td>
</tr>
<tr>
<td>B&amp;C,Edge-36</td>
<td>8</td>
<td>330.7 (22.3)</td>
<td>2.87 (.69)</td>
<td>17.44 (1.1)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

Table 3.6. Flexural test results for 30% CFRPEEK A&D HFBs after 36 weeks exposure to 10% serum. Control indicates those HFBs that were tested in the characterization section.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&amp;D-Control</td>
<td>34</td>
<td>269.4 (37.6)</td>
<td>3.58 (.48)</td>
<td>12.1 (2.9)</td>
</tr>
<tr>
<td>A&amp;D-36 wks</td>
<td>25</td>
<td>265.7 (45.7)</td>
<td>3.21 (.34)</td>
<td>12.2 (2.6)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>A&amp;D,Near -C</td>
<td>16</td>
<td>244.5 (30.9)</td>
<td>3.78 (.47)</td>
<td>10.31 (2.03)</td>
</tr>
<tr>
<td>A&amp;D,Near-36</td>
<td>12</td>
<td>239.7 (45.7)</td>
<td>3.22 (.36)</td>
<td>10.79 (2.42)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>A&amp;D,Away -C</td>
<td>16</td>
<td>295.57 (26.8)</td>
<td>3.33 (.36)</td>
<td>13.96 (2.66)</td>
</tr>
<tr>
<td>A&amp;D,Away-36</td>
<td>12</td>
<td>290.3 (32.3)</td>
<td>3.23 (.34)</td>
<td>13.41 (2.31)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>
Figure 3.13. Flexural test results of Y MFBs and Y, B&C MFBs after 0 and 36 weeks exposure to 10% serum.
Figure 3.14. Flexural test results of Z MFBs and Z, A&D MFBs after 0 and 36 weeks exposure to 10% serum.
Figure 3.15. Flexural test results of All MFBs and B&C MFBs (both Y and Z) after 0 and 36 weeks exposure to 10% serum.
Figure 3.16. Flexural test results of A&D MFBs (both Y and Z) after 0 and 36 weeks exposure to 10% serum.
Table 3.7. Flexural test results for 30% CFRPEEK Y MFBs after 36 weeks exposure to 10% serum. Control indicates those MFBs that were tested in the characterization section.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-Control</td>
<td>44</td>
<td>285.4 (28.5)</td>
<td>3.17 (.52)</td>
<td>14.1 (2.9)</td>
</tr>
<tr>
<td>Y - 36wks</td>
<td>27</td>
<td>295.7 (26.0)</td>
<td>2.92 (.42)</td>
<td>14.7 (2.1)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Y,B&amp;C-Control</td>
<td>27</td>
<td>297.2 (22.0)</td>
<td>2.84 (.25)</td>
<td>15.6 (2.3)</td>
</tr>
<tr>
<td>Y,B&amp;C-36 wks</td>
<td>18</td>
<td>301.1 (23.6)</td>
<td>2.87 (.49)</td>
<td>15.3 (2.0)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Y,B&amp;C,Core-C</td>
<td>22</td>
<td>293.4 (20.0)</td>
<td>2.69 (.25)</td>
<td>15.0 (1.9)</td>
</tr>
<tr>
<td>Y,B&amp;C,Core-36</td>
<td>14</td>
<td>296.0 (23.6)</td>
<td>2.79 (.24)</td>
<td>14.9 (2.1)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Y,B&amp;C,Edge-C</td>
<td>5</td>
<td>313.8 (25.1)</td>
<td>2.65 (.16)</td>
<td>18.1 (2.1)</td>
</tr>
<tr>
<td>Y,B&amp;C,Edge-36</td>
<td>4</td>
<td>119.0 (13.9)</td>
<td>3.14 (.96)</td>
<td>16.8 (1.2)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

Table 3.8. Flexural test results for 30% CFRPEEK Z MFBs after 36 weeks exposure to 10% serum. Control indicates those MFBs that were tested in the characterization section.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-Control</td>
<td>40</td>
<td>279.6 (47.3)</td>
<td>3.09 (.49)</td>
<td>13.48 (3.26)</td>
</tr>
<tr>
<td>I - 36wks</td>
<td>21</td>
<td>275.4 (49.5)</td>
<td>3.15 (.41)</td>
<td>12.90 (3.52)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Z,A&amp;D-Control</td>
<td>16</td>
<td>267.3 (42.6)</td>
<td>3.48 (.51)</td>
<td>11.87 (2.94)</td>
</tr>
<tr>
<td>Z,A&amp;D-36 wks</td>
<td>13</td>
<td>263.5 (35.5)</td>
<td>3.36 (.33)</td>
<td>11.76 (2.57)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Z,A&amp;D,Away-36</td>
<td>7</td>
<td>277.1 (30.8)</td>
<td>3.34 (.35)</td>
<td>12.91 (2.27)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Z,A&amp;D,Near-C</td>
<td>8</td>
<td>239.5 (37.9)</td>
<td>3.75 (.56)</td>
<td>9.91 (2.28)</td>
</tr>
<tr>
<td>Z,A&amp;D,Near-36</td>
<td>6</td>
<td>247.6 (36.4)</td>
<td>3.37 (.33)</td>
<td>10.41 (2.38)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>
MFBs from sections B&C, B&C edge MFBs or B&C core MFBs. The same was true for A&D MFBs, A&D MFBs located away from the gate, and A&D MFBs located near the gate (Figure 3.14 and Table 3.6). Since the AY MFBs and the BZ MFBs were tested at 18 weeks, B&C bars from the Y MFBs were evaluated and A&D bars from the Z MFBs were evaluated for potential differences in flexural properties. Figures 3.15 and 3.16 (and Tables 3.7 and 3.8) illustrate that the flexural properties remained invariant.

3.3.3. Enhanced Degradation - CFRPEEK: Scanning electron micrographs taken of the fracture surfaces of CFRPEEK MFBs that had been continuously stressed in serum for 18 weeks were not noticeably different from the micrographs of the 18 week or 36 week exposed fracture surfaces.

3.3.4. 36 weeks - Continuous Fiber/PEEK: The average percent increase in weight of the MFBs cut longitudinally was 0.545 and the average percent change in weight of the MFBs cut transversely was 0.400 (Table 3.9). These weight gains are greater than that observed for the chopped PEEK composite. This may indicate an absorption of fluid that is not matrix dominated. If there is poor fiber-matrix bonding, fluid would wick up the interface. This phenomena would be greater for the MFBs that had a greater number of fiber ends exposed, as would be the case with the transverse MFBs. Differences were not seen between the flexural properties of either the exposed
Table 3.9. Percent weight change of continuous fiber reinforced PEEK MPBs after 36 weeks exposure to 10% serum.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Average</th>
<th>Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-Control</td>
<td>10</td>
<td>0.01039</td>
<td>0.00420</td>
</tr>
<tr>
<td>Longitudinal</td>
<td>10</td>
<td>0.54505</td>
<td>0.17468</td>
</tr>
<tr>
<td>Trans-Control</td>
<td>10</td>
<td>0.01989</td>
<td>0.00438</td>
</tr>
<tr>
<td>Transverse</td>
<td>10</td>
<td>0.40020</td>
<td>0.15528</td>
</tr>
</tbody>
</table>

Table 3.10. Flexural test results of longitudinal (L) and transverse (T) continuous fiber reinforced PEEK MPBs after 0 and 36 weeks exposure to 10% serum.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Control</td>
<td>10</td>
<td>1647.7 (35.3)</td>
<td>3.05 (.40)</td>
<td>107.6 (6.0)</td>
</tr>
<tr>
<td>L - 36wks</td>
<td>10</td>
<td>1660.4 (133.0)</td>
<td>3.22 (.13)</td>
<td>103.8 (4.7)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>T-Control</td>
<td>10</td>
<td>158.6 (12.0)</td>
<td>1.85 (.20)</td>
<td>10.10 (.46)</td>
</tr>
<tr>
<td>T - 36wks</td>
<td>10</td>
<td>147.4 (16.1)</td>
<td>1.72 (.23)</td>
<td>10.03 (.83)</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>
longitudinal MFBs or the exposed transverse MFBs compared to the control MFBs (Table 3.10).

3.3.5. 36 weeks - 30% CFRP Polysulfone: The average percent weight gain of the CFRPSU MFBs cut from section A was 0.749, and the average percent weight gain of the CFRPSU MFBs cut from section B was 0.759. This is significantly greater than what was observed for the other composites. The average flexural stress for both sections A and B increased after 36 weeks exposure to 10% serum compared to the control bars (Table 3.12). Although this is contrary to what has been reported in the literature, a closer examination of the microstructure of the CFRPSU MFBs indicated a possible explanation. Shown in Figure 3.17 are light micrographs of the tensile surfaces of a control CFRPSU MFB (5B) and of an exposed CFRPSU MFB (5B). Pores are evident on both surfaces of the bendbars, the pores of the control MFB being slightly larger than that of the exposed MFB. The presence of these pores would change the flexural behavior compared to a composite that was processed without pores.
Table 3.11. Percent weight change of 30% chopped carbon fiber reinforced Polysulfone MFPs after 36 weeks exposure to 10% serum.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Average</th>
<th>Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-Control</td>
<td>9</td>
<td>0.18246</td>
<td>0.02535</td>
</tr>
<tr>
<td>A - 36wks</td>
<td>9</td>
<td>0.74904</td>
<td>0.08874</td>
</tr>
<tr>
<td>B-Control</td>
<td>9</td>
<td>0.19619</td>
<td>0.00640</td>
</tr>
<tr>
<td>B - 36wks</td>
<td>9</td>
<td>0.75895</td>
<td>0.13841</td>
</tr>
</tbody>
</table>

Table 3.12. Flexural testing results for 30% CFRPSU after 36 weeks exposure to 10% serum. Literature values for PSU (Rubin, 1990) and 30% CFRPSU (manufacturer’s data -Hastings, 1988 and *data from Hastings MS Thesis, 1988) are given for comparison. Numbers in parenthesis are standard deviations.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-control</td>
<td>9</td>
<td>159.6 (13.3)</td>
<td>2.47 (.24)</td>
<td>8.52 (1.38)</td>
</tr>
<tr>
<td>A - 36wks</td>
<td>9</td>
<td>174.9 (14.0)</td>
<td>2.29 (.25)</td>
<td>9.79 (1.25)</td>
</tr>
<tr>
<td>p-value</td>
<td>.0298</td>
<td>NS</td>
<td>.0575</td>
<td></td>
</tr>
<tr>
<td>B-control</td>
<td>9</td>
<td>167.6 (11.8)</td>
<td>2.39 (.17)</td>
<td>8.97 (1.23)</td>
</tr>
<tr>
<td>B - 36wks</td>
<td>9</td>
<td>183.3 (15.5)</td>
<td>2.25 (.17)</td>
<td>10.33 (.76)</td>
</tr>
<tr>
<td>p-value</td>
<td>.0281</td>
<td>NS</td>
<td>.0123</td>
<td></td>
</tr>
<tr>
<td>Polysulfone (Udeell)</td>
<td></td>
<td>106</td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>PSU/30%C</td>
<td></td>
<td>220</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>*PSU/30%C</td>
<td></td>
<td>178</td>
<td></td>
<td>10.5</td>
</tr>
</tbody>
</table>
Figure 3.17. Light micrographs of the microstructure close to the fracture surface of CFRPSU MFBs. Pores are visible in both a) the unexposed MFBs and b) the MFBs exposed to 10% serum for 16 weeks.
3.4. Discussion

It was attempted to have each CFRPEEK MFB be its own self-control by monitoring the bending modulus obtained by testing the MFBs at low loads (below the elastic load limit). Moduli calculated with this method, although consistent, were greater than moduli calculated when the MFBs were tested to failure, even for the MFBs that had not been exposed to serum (Table 3.9). Although each CFRPEEK MFB was loaded to 17 N either twice (Z MFBs) or four times (Y MFBs) before being tested to failure, it was not expected that fatigue of the MFBs should have caused the lower modulus values. The load for modulus testing was selected to be well within the elastic, reversible region of the CFRPEEK stress/strain curves. At this load (which corresponds to 80 MPa for a 1 x 5 x 30 mm specimen), the number of cycles to failure due to fatigue would be in the millions (ICI, 1986). In addition, pretesting three samples for 13 or 15 times did not show a decrease in modulus (Figure 3.6).

Another possibility for the discrepancies between moduli may simply be due to experimental error. The load deflection curves that are generated for many MFBs had a "toe" region in the beginning that does not represent a property of the material. It is an artifact caused by alignment or seating of the specimen (D790M). Since only a small part of the load/deflection curve was generated for modulus testing, it is possible that this artifact was not fully accounted for. There were also no significant differences between the modulus values calculated at failure for the precycled MFBs versus modulus of
MFBs cut from the same positions. This is further evidence that the higher pretest modulus values may be artifactual.

The lack of degradation in the flexural properties of either the 30%CFRPEEK or continuous fiber reinforced PEEK exposed to 10% serum at 37°C for 18 or 36 weeks is similar to the results found for CFRPEEK exposed to saline at 37°C for 3 weeks (Brown et al., 1990), Ringers solution at 37°C for 1.8 years (Maharaj et al., 1991), or boiling water for 340 days (Kwarteng and Stark, 1990).

The weight change of the composite PEEK MFBs soaked in 10% serum was similar to, though slightly higher than, the weight changes observed for other neat and composite PEEK specimens exposed to water or saline. In the present study a 0.35% to 0.40% weight increase was observed for the 30%CFRPEEK MFBs after 18 and 36 weeks exposure. A 0.40% weight change was observed for the transverse continuous fiber PEEK and a 0.54% weight change was found for the longitudinal PEEK after 36 weeks. In comparison, the moisture uptake of neat PEEK after 66 days immersion in water at 35°C was 0.44% (Grayson and Wolf, 1987). This increased to 0.55% when the samples were kept at 95°C for 410 days. In 100% relative humidity the maximum moisture content in neat PEEK was found to be 0.3% and for APC-2 composite 0.1% at 140°F (Wang and Springer, 1989). The moisture absorption of an APC-2 laminate placed in Ringer's solution at 37°C reached an equilibrium value of 0.28% and remained at this level for 639 days (Maharaj et al., 1991). However, at 90°C the moisture content was 0.33% after approximately 120 days, remained constant for 200 days, and then
began rising again to a level of 0.44% at the end of the 541 day test period. In contrast an evaluation of APC-2 composites after immersion in boiling water for 340 days showed a moisture uptake of 0.3% (Kwarteng and Stark, 1990).

The lower sorption in the chopped fiber composite compared to the continuous fiber composite may indicate that in addition to matrix sorption, the fiber matrix interface, especially of the continuous fiber composite, may be an area susceptible to absorption as well. Also, the use of 10% serum introduced many more components that may influence fluid uptake by the composite. In addition to cations such as sodium, potassium, calcium, and magnesium and anions such as chlorine, bicarbonate, phosphate, serum also contains sulfate, amino acids, glucose, urea, lactate, creatine, enzymes, lipids, fatty acids, cholesterol, lipoproteins, glycoproteins and vitamins (Geigy, 1975; Guyton, 1991). The major proteins in serum include albumin and globulins (α, α1, α2, β, gamma). The average molecular weight of albumin is approximately 69,000 and of the globulins approximately 140,000 (Guyton, 1991). Although the proteins are too large to diffuse into the PEEK matrix, they may be absorbed onto the surface. If this occurs, the diffusion of water and other small components of serum may be altered.

Evaluating the fracture surfaces of the 30%CFRPEEK MFBs with SEM to look for any effect of fluid sorption was difficult. Uncoated fibers, debonding of the fiber from the matrix, and increased matrix plasticity have all been implicated as possible effects of moisture
sorption (Agarwal and Broutman, 1980). All of these telltale signs were discovered, to one degree or another, in the fracture surfaces of the unexposed 30%CFRPEEK MFBs. Therefore, dissecting out any effects due to exposure from the characteristic unexposed fracture surface proved impossible. Even after examining the fracture surfaces of the 30%CFRPEEK MFBs from the enhanced degradation experiment, a difference could not readily be deciphered. For future degradation studies it may be necessary to increase the strain rate of the experiment in order to achieve a fracture surface that is primarily indicative of brittle fracture. Then effects such as plasticizing the matrix may become more evident.

For the continuous fiber reinforced PEEK MFBs, the issues that were examined for characterizing the chopped fiber MFBs, such as the possibility of a size effect, were not examined. In addition, although it is recommended (D790M) that a 60:1 span to depth ratio be used to evaluate bending modulus, this was not done. Therefore, the flexural properties of the continuous-fiber composite MFBs are valid only relative to each other to determine the effect of exposure on properties. Until more in depth characterization is completed, the properties calculated should not be compared to the flexural properties of larger standard size specimens.

The polysulfone composite MFBs were the only ones to be effected by exposure to the 10% serum at 37°C for 36 weeks. The results observed were contrary to what was expected. Based on exposure studies of CFRPSU saline (Brown et al., 1990) and in
Ringer's solution (Maharaj et al., 1991) it was thought that the flexural properties of the exposed MFBs would decrease. The opposite occurred. Flexural strength increased, bending modulus increased, and strain decreased. This appeared to be an embrittling or anaplastic effect. Upon closer look at the microstructure of the CFRPSU MFBs it was found that the composite was poorly processed and pores were evident. A study was not undertaken to examine if pores were present in every MFB, but in many of the MFBs, both control and exposed, pores were observed (Figure 3.17). The presence of these pores may also account for the high % weight change in this composite (0.75%) compared to the PEEK composite. Another indication that the pores are effecting flexural results is that the flexural strength (160 MPa) and modulus (8.5 GPa) of the MFBs as well as that of the intact bars (178 MPa and 10.6 GPa) (Hastings, 1988) are much less than the quoted literature values of 220 MPa and 14 GPA (Udel) for this material. In addition the decrease in strength and modulus of the unexposed MFBs compared to the intact bendbar may be a result of the relative increase in the size of the pores compared to the specimen dimensions. To adequately understand the significant difference found between the exposed CFRPSU MFBs and the unexposed MFBs a more complete investigation into the pore size and distribution within and between the control and exposed MFBs is necessary.
4. Particles

4.1. Introduction: As a 20th century Archimedes may have shouted "Eureka" upon discovering the unlimited possibilities for polymer composites in orthopaedics, he soon would have met his friend Achilles muttering about polymer particles. For every "Eureka" there tends to be an Achilles' heel. And so it is with orthopaedic composites. The problem is an old one that has yet to be conquered. It centers around UHMWPE used in a variety of orthopaedic implants, primarily as a bearing surface. Particulate UHMWPE debris generated from implant wear and liberated into the surrounding tissue is being implicated as a cause for implant loosening and osteolysis (Charnley, 1970). Problems with polymeric particles causing adverse tissue responses did not begin with polyethylene, nor are they likely to end with polyethylene. Unless the wear resistance of any new polymers, including composite matrix polymers, is 100%, there is a strong likelihood that polymeric debris will be generated in certain applications.

Polymers that were first used in bearing surfaces of early hip implants included polymethylmethacrylate (PMMA), polytetrafluoroethylene (PTFE), polyacetal and polyamides. The poor wear resistance of these polymers combined with a severe tissue reaction to the generated particulate debris required replacement of these materials with ones that had better wear properties. Polyethylene, either high density (HDPE) or ultra high molecular weight (UHMW) was the choice.
The biological response to bulk polyethylene in soft tissue and bone has been well characterized through clinical use and research studies. It is typically used as a negative control in studies determining the cellular response of the biocompatibility of a potential material. This "proven inertness" of polyethylene as well as its good wear properties have been prime factors for its use in total joint prostheses. The response elicited by polyethylene in particulate form, however, is distinctly different from the response of the material in bulk form (Goodman et al., 1988). The use of UHMWPE as a bearing material in hip and knee implants has been very successful, although not completely so. The creep and wear properties of UHMWPE may limit the longevity of prostheses made with polyethylene (Farling and Greer, 1980).

Attention to the role of wear debris in implant loosening has focused on the tissue response to metal, bone cement and polyethylene particles. Microscopic analysis of tissue from implant retrievals has shown a granulomatous tissue response with smaller particles being phagocytized and the larger particles surrounded by foreign body giant cells (Willert and Semlitsch, 1977). This corresponds with a synovial-like membrane which can lead to implant loosening (Goldring et al., 1983). Much effort has been spent in attributing this response primarily to either metal (Rae, 1975; Agins et al., 1988; Goldring et al., 1990) or PMMA (Harris et al., 1976; Jasty et al., 1986; Jones et al., 1987). More and more evidence, however, is surfacing implicating polyethylene particles.
In vitro studies have demonstrated that polyethylene particles, in and of themselves, can be responsible for bone resorption. In one study (Howie et al., 1988), using a rat model, a plug of PMMA was placed in the distal part of the femur next to the knee joint. This plug was not subjected to any mechanical stresses. Polyethylene particles, 20-200 µm were injected into the joint. The opposite femur served as a control with the plug implanted but without the injected particles. The results showed no bone resorption at the control femur, but active resorption of bone around the PMMA implant in the joint with the UHMW particles. The bone was replaced by cellular connective tissue. Another study examined the effects of polyethylene particles (16-67µm) implanted in rabbit tibia (Goodman et al., 1990). In this report as well, the histological reaction stimulated by the polyethylene particles was found to resemble the membrane surrounding loose joint arthroplasties. Although these studies are important in exhibiting that polyethylene particulate debris can incite an unfavorable tissue response, the large size of the particles used as well as the high concentration of particles may not be clinically relevant. Evidence suggests that a great amount of polyethylene debris present in joint spaces is in the submicron range which is not visible in the light microscope (Kossovsky et al., 1991, 1992). Furthermore, the presence of polyethylene particles and an associated macrophage response even in THAs that are solidly fixed and exhibit a minimal amount of wear has been shown (Howie et al., 1990). Polyethylene particles, as well as metal and PMMA particles,
may also be transported via lymphatics to lymph nodes draining the joint (Gray et al., 1989; Willert and Semlitsch, 1977; Bauer et al., 1992).

The tissue response incited by polyethylene wear particles can be expected to be observed in various degrees by other polymeric particles as well, including those polymers used as matrix materials in composites. In addition to the polymer, another source of possible particulate debris is the reinforcing carbon fiber. Carbon particles up to 8 µm have been implanted intra- and periarticularly in rats (Helbing et al., 1980). Particle deposits were seen in synovial cells, although giant cells were not observed. Numerous particles were found in the perivascular lymphatic spaces, and giant cells were observed. The regional lymph nodes also contained deposits of carbon with associated macrophages and giant cells. The long term effects of carbon fibers and carbon particles was examined in rats (Tayton et al., 1982). Carbon debris from fiber breakage was found in phagocytic cells and near lymphatic vessels. Occasional giant cells and granulation tissue was also seen. This response was also observed for the carbon powder. An interesting comment has been made that the reaction of tissues to carbon fiber within the joint is less favorable than to carbon fiber extra-articularly (McKibbin, 1984). Evidently, carbon particles can also activate macrophages and giant cells as well.

A composite that has been in clinical use is Poly-2. Poly-2 consists of UHMWPE reinforced with carbon fibers. It has been used
as the bearing surface in acetabular cups and tibial plateaus.

UHMWPE was reinforced with 10 wt% high tensile strength low modulus carbon fibers which were approximately 1.5 mm long with a major diameter of 15 μm and a minor diameter of 6 μm (Farling and Greer, 1980). Fiber orientation and distribution within the UHMWPE was random. The composite was compression molded directly into the final prosthesis shape. Reinforcing polyethylene with fibers increased the strength and stiffness of the composite greater than that of polyethylene alone even though poor bonding between the fibers and the matrix was noted (Farling and Greer, 1980).

This composite was developed to provide better wear resistance than that afforded by UHMWPE. Indeed, results indicating that wear rates of the Poly-2 composite in a hip simulator and a multiple motion tester (to simulate knee wear) were better than that of UHMWPE (Farling and Greer, 1980) have been presented. These results were in sharp contrast to another study which demonstrated that wear of Poly-2 was 1.8 times greater than that of UHMWPE (McKellop et al., 1981). It was also shown that increasing the stiffness of the composite also decreased contact area and therefore increased contact stresses between the tibial or acetabular bearing surface and the apposing femoral component (Wright et al., 1981). These stresses were shown to be greater than the compressive strength of the composite under certain physiological situations (Wright et al., 1981). Significantly this indicated that deformation and wear formerly thought to be decreased in the composite compared to UHMWPE
may actually be increased because of the magnification of contact stresses. This was not known, however, when Poly-2 materials were first used clinically.

Poly-2 was developed for use in several total joint replacement prostheses, and implantation in humans began in 1975 (Halcomb and Bardos, 1981). The biological response to HDPE particles implanted in mice knee joints compared to the response to carbon fiber reinforced HDPE was stated to be identical with the carbon fiber component not appearing to modify the response (Rushton, 1984). Case studies of retrieved Poly-2 implants indicated gray staining of synovial tissue with significant amounts of polyethylene and carbon wear debris present (Groth and Shilling, 1983). Histologically, the carbon appeared well tolerated in contrast to the significant granulomatous reaction found with the polyethylene. This situation of the presence of polyethylene and composite wear debris associated with aseptic loosening of the implant has been repeatedly reported for patients with Poly-2 implants (Dannenmaier et al., 1985; Wright et al., 1988; Rosenthall, 1987). However, a noticeable increase in damage of Poly-2 components compared to UHMWPE components was not found (Wright et al., 1988).

With the clinical history of composite Poly-2, an opportunity to gain information as to how composites may perform in structural applications is available. Specifically, composite wear debris generated in vivo can be studied. Evaluating wear debris is a challenge however, and present methods which relate particle types,
sizes and shapes to an associated biological response are limited.

Light microscopic examination of stained histological sections of retrieved tissue around implants is the primary method for determining the biological response to particulate materials. Although this method is very useful, it is limited. For instance, the minimum size of particles that can be detected with the light microscope is in the micron range. Submicron particles are below the limit of resolution. Because of this, many studies evaluating the biological response to particles only use particles that are greater than 1 micron, usually much more so (Howie et al., 1988; Goodman et al., 1990; Rushton and Rae, 1984). There is also a possibility that the particles generated for studying the biological response to wear debris may actually include a submicron fraction that is not visible, and therefore is ignored.

Some unique methods have been used to examine submicron particles. Examination of the biological response of submicron size carbon particles in rats was done by particle radiolabelling (More et al., 1988). These particles were found to be well tolerated in vivo. Transmission electron microscopy has also been used to examine the submicron particulate in tissue sections (Sheffield, 1986). Additionally, photon correlation spectroscopy has been used to count submicron particulate digested from tissue (Kossovsky et al., 1992).

Identifying the composition of particles present in tissue is also difficult. Currently, the primary materials to be found in total joint implants are cobalt chromium, titanium, polyethylene, and
polymethylmethacrylate. Metal appears black by light microscopy. Differentiating between metals in the same tissue is impossible with light microscopy. With the advent of composite materials, discerning between carbon and metal is also impossible, unless the carbon retains its fiber shape. Polyethylene can usually be identified using polarized light. The very smallest polyethylene particles are difficult to recognize and are sometimes overlooked. An Oil Red O stain has been developed to assist in identifying polyethylene (Campbell et al., 1992; Peters et al., 1991, 1992). Although sensitive, this stain is not specific. Intracellular lipids will also be stained with Oil Red O (Bauer, 1992). Due to histological processing, PMMA is dissolved out of the tissue. Therefore, PMMA is recognized by apparent vacuoles in the stained section. As more and more evidence implicates particles and the associated biological response to implant failure, additional information, that can not be learned from light microscope sections, is required.

Particles that are generated from implant designs in current use as well as particles that may be generated from prospective composite devices, have specific sizes, shapes and surface characteristics. To examine these features as well as to determine concentrations of particles, techniques to retrieve particles from tissue are now being developed. In order to extract foreign particles from tissue, a digestion protocol that dissolves only tissue and not particles is necessary. Several research groups have attempted this, using strong bases (Kossovsky et al., 1991; Campbell,
1992) or a commercial tissue solubilizer (Lee et al., 1992). Proof that these protocols actually isolate the desired particles in their original shapes and sizes is not apparent. Once a tissue digestion protocol is refined or redefined, the recovered particles can be evaluated.

These methods, histological evaluation and tissue digestion, are pertinent for evaluating materials already in clinical use. The relative contribution from particle size, number, morphology and composition to the overall biological response to the Poly-2 wear debris may be discovered in the histopathology of clinical retrievals. Modeling the clinical situation in vitro and in vivo to study the biological response to wear products of candidate composite implants is a challenge. Difficulty has arisen with generating particles that would be representative of particles present clinically. In several studies, particles used for implantation (Howie et al., 1988; Goodman et al., 1990) or cell culture (Boyd et al., 1984; Horowitz et al., 1991) are not wear products, but rather are powders or beads used in processing. Other studies have used particles generated by wear (Emmanual et al., 1990), although it is debatable if these particles are representative of what is released clinically, since the surface chemistry is altered by cleaning and sterilization before implantation.

Techniques for creating particles include hip simulators (Rae, 1979) and attrition techniques (Leigh et al., 1992). A procedure to produce and introduce metallic wear particles directly into cell
culture has been developed (Brown and Merritt, 1985; Merritt et al., 1990). This method utilizes a fretting simulator described in ASTM Standard F 897. Wear debris is created from the micromotion of a screwhead against a countersink. With the characterization of the composite particles generated with this methodology and comparison to those particles seen clinically, the biological response to polymer composite wear debris can be more completely understood.

The objective of this study was to evaluate the degradation products resulting from mechanical wear of Poly-2 and PEEK composites. Specifically, the following aims were investigated: 1) to compare particles observed in histology slides with particles obtained by tissue digestion and to examine the biological response to Poly-2 particles; 2) to compare Poly-2 particles generated in vitro with Poly-2 particles generated in vivo; and 3) to compare composite PEEK particles generated in vitro with Poly-2 particles generated in vitro.
4.2. Materials and Methods: The methods developed and used can be loosely divided into four parts. In the first sections, 4.2.1. through 4.2.5., methods for the development and validation of a protocol for the extraction of particles (wear debris) from tissue surrounding a Poly-2 implant are presented. The second part, section 4.2.6., describes the methods for the in vitro generation and isolation of wear debris. The third part, sections 4.2.8. through 4.2.10., comprise methods for analyzing particles. Lastly, sections 4.2.11 through 4.2.13 describe the methods for accomplishing the specific aims outlined in the introduction.

4.2.1. Tissue Retrieved from Patients with Poly-2 Implants for Particle Extraction and Analysis: In order to examine wear particles that were generated in vivo, synovial tissue from patients that had undergone revision surgery was obtained from University Hospitals (U.H.) (Table 4.1). Retrieved tissue was acquired in two states: unfixed frozen (usually frozen 1-7 days after retrieval) or fixed in formalin.

The tissue in formalin from U.H. was kept in a bucket that originally contained the retrieved implant. Tissue was selected from four patients (lab #282, #286, #324, #359) and sent to U.H. pathology to be embedded in paraffin. Tissue blocks and three slides from each block were returned. Previous slides from the same patient’s tissue were also available, although the associated paraffin blocks were not.
Table 4.1. Tissue that was used in digestion experiments. The state of the tissue that was available, and the implant materials associated with the tissue are listed.

<table>
<thead>
<tr>
<th>Lab #</th>
<th>State of tissue</th>
<th>Implant</th>
</tr>
</thead>
<tbody>
<tr>
<td>248</td>
<td>unfixed</td>
<td>fem: Ti tib: P2/Ti pat: P2/Ti</td>
</tr>
<tr>
<td>282</td>
<td>unfixed formalin paraffin</td>
<td>fem: Ti tib: P2/Ti pat: P2/Ti</td>
</tr>
<tr>
<td>286</td>
<td>unfixed formalin paraffin</td>
<td>fem: CoCr tib: P2/Ti pat: P2/Ti</td>
</tr>
<tr>
<td>297</td>
<td>unfixed</td>
<td>fem: Ti tib: P2/Ti pat: P2/Ti</td>
</tr>
<tr>
<td>324</td>
<td>formalin paraffin</td>
<td>fem: Ti acet: P2</td>
</tr>
<tr>
<td>359</td>
<td>unfixed formalin paraffin</td>
<td>fem: Ti tib: P2/Ti pat: PE/Ti</td>
</tr>
</tbody>
</table>
The frozen tissue from U.H. was not suitable for paraffin embedding since it was not fixed at retrieval or frozen immediately. Slides from tissue previously embedded from the same patient were available, although the associated paraffin blocks were not.

4.2.2. Preparation of Tissue for Freeze Drying: Tissue for digestion was first dehydrated by freeze drying. The primary advantage of dried tissue over wet tissue is the minimization of variability in tissue weight (and subsequently particle concentration) associated with wet (hydrated) tissue. In addition, dried tissue samples are easier to store. Preparation of tissue for freeze drying depended on the state of the tissue.

Unfixed Tissue: If tissue was unfixed, the tissue was kept frozen until cut for drying. Cut tissue was then refrozen.

Formalin Fixed Tissue: If tissue was fixed in formalin, selected pieces were cut, approximately 1 cm³, and washed in filtered distilled water. Tissue was removed from the water and frozen.

Paraffin Embedded Tissue: If tissue was embedded in paraffin, the section of the tissue that was to be digested (determined by microscopically examining slides cut from the block) was cut from the block with a razor blade. Excess paraffin was removed by deparaffinizing using xylene for approximately 24 hours at room temperature. Heating the xylene in a 50°C oven (Blue M) for a few hours was found to be helpful, especially if the tissue sample was large. The tissue was then soaked in 100% ethanol. Tissue was
rehydrated in decreasing concentrations of ethanol (70%, 40%) for approximately 1 hour for each concentration and finally placed in 100% distilled, deionized water. Tissue was removed and frozen.

4.2.3. Freeze Drying: Tissue was freeze-dried using a lyophilizer (VirTis). Frozen tissue samples were placed in 125 mm filter flasks (one flask for each tissue sample). The top of the flasks were covered with laboratory film (parafilm). These flasks were put in the freezer for at least one hour. The vacuum pump and the refrigeration system of the lyophilizer were turned on. When the condenser temperature dropped below 0°C the flasks were connected to the "quickseal" arms of the lyophilizer. A small amount of vacuum grease was used to coat the neck of the flask and a number 5 rubber stopper was inserted. The vacuum line was opened while holding onto the rubber stopper (to avoid having the stopper being sucked in too far which can cause the neck of the flask to break). Tissue was dried for at least 4 hours.

The dried tissue was cut with a razor blade, and 0.02-0.03 grams were weighed out on a microbalance (Mettler AE163). Weighed tissue was placed in a 10 ml polystyrene twist cap tube (Falcon 2027).

4.2.4. Development of a Tissue Digestion Protocol for Particle Recovery and Analysis: The development of a digest protocol necessitated both the choice of an appropriate digest agent as well
as the determination of a method for particle collection and suspension. Several questions permeated the decisions in developing a digest procedure. What are the time and temperature required for complete digestion? Are repeated digestions required, that is does more chemical need to be added before the digest is complete? Is the digest complete with only non-biological particles remaining after digestion? What subsequent steps are required after digestion of the tissue to extract and prepare the particles for analysis?

4.2.4.1. Determination of Appropriate Digest Agent for Particle Extraction from Synovial Tissue: All of the chemicals or solutions used in digestion (except for concentrated nitric acid) were prefurred with a 0.45 μm, 25 mm diameter disposable filter assembly (Acrodisc, Gelman Sciences), which fitted to the end of a 10 or 20 cc syringe.

Several chemicals were considered for digesting the tissue: sodium hypochlorite (Chlorox); 2N sodium hydroxide (NaOH); and nitric acid including concentrated HNO₃ (70%), 35% HNO₃ and 17% HNO₃.

To evaluate the efficacy of digestion by each digest agent, approximately 0.02 - 0.03 grams of dried synovial tissue or 0.2-0.3 grams wet tissue was exposed to the digest agent. The volume of agent used and the time required for digestion at room temperature or at an elevated temperature was recorded. It was also noted if repeated exposure to the digest agent was required for complete digestion of the tissue. Generally, between 0.5 and 1.5 ml of digest
agent was added to the dried tissue, and to the wet tissue up to 3 ml of digest agent was used.

4.2.4.2. Determination of Methods for Particle Collection: Once digested, methods for collecting the particles from the digest solution and for resuspension of the particles in a solution that can be used in Coulter analysis as well as be filtered for SEM and light microscopy were examined.

To collect only metal particles and carbon fiber particles which have densities of 4-9 g/cm$^3$ (depending on the metal) and 1.77 respectively, direct centrifugation of the digest solution was performed. This was possible since these particles sank in either 2N NaOH or concentrated nitric acid (Table 4.2.) (sodium hypochlorite was not used since the results from section 4.2.4.1. indicated poor digestion). UHMWPE, however, has a density between 0.94 and 0.98 g/cm$^3$. This is less than the density of the prospective digest agents (Table 4.2.). Therefore, polyethylene particles floated in the digest solution. In order to sink the polyethylene and draw off the solution by centrifugation, the following methods for lowering the density of the digest solutions were evaluated.

It was first determined if the density of 2N NaOH and concentrated HNO$_3$ could be successfully decreased by combining the acid and base with a lower density liquid, particularly ethanol which has a density of 0.789 g/cm$^3$. Table 4.3. lists the ethanol/digest agent solutions that were used in an attempt to lower the density of
Table 4.2. Density of chemicals and materials.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric Acid (100%)</td>
<td>1.503</td>
</tr>
<tr>
<td>Concentrated HNO₃ (70%)</td>
<td>1.352</td>
</tr>
<tr>
<td>Sodium Hydroxide Solid</td>
<td>2.130</td>
</tr>
<tr>
<td>2 Normal NaOH</td>
<td>1.084</td>
</tr>
<tr>
<td>Ethanol (CH₃CH₂OH)</td>
<td>0.789</td>
</tr>
<tr>
<td>Methanol (CH₃OH)</td>
<td>0.791</td>
</tr>
<tr>
<td>Hemosiderin Fe₂O₃-Fe(III)oxide</td>
<td>5.24</td>
</tr>
<tr>
<td>Fe₂O₃ hydrate</td>
<td>2.44-3.60</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>0.94-0.98</td>
</tr>
<tr>
<td>PEEK (amorphous)</td>
<td>1.263</td>
</tr>
<tr>
<td>PEEK (crystalline)</td>
<td>1.401</td>
</tr>
<tr>
<td>Carbon fiber (Hercules AS4)</td>
<td>1.770</td>
</tr>
<tr>
<td>CoCrMo (Cast)</td>
<td>8.3</td>
</tr>
<tr>
<td>CoCrMo (Wrought)</td>
<td>9.2</td>
</tr>
<tr>
<td>Ti (CP)</td>
<td>4.5</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3. Density of Solutions

<table>
<thead>
<tr>
<th>Substance</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 N NaOH : 100% EtOH 1 : 2</td>
<td>0.888</td>
</tr>
<tr>
<td>conc. HNO₃ : H₂O : 100% EtOH 1 : 2 : 16</td>
<td>0.850</td>
</tr>
</tbody>
</table>
the solution to that below the density of UHMWPE. Since NaOH is miscible with ethanol, 100% ethanol was added directly. In contrast, concentrated HNO₃ reacts violently with the addition of 100% ethanol. Therefore, direct addition of ethanol was not possible. Two methods were examined to circumvent this. First, the acid was neutralized with a base (NaOH), and then ethanol was added (Table 4.3.). In the second method, the concentrated acid was first diluted to 17% concentration before the addition of ethanol (Table 4.3.).

Once the density was lowered, the particle solution was centrifuged for 30 minutes (2500 RPM - IEC International portable refrigerated centrifuge). The supernatant was drawn off and discarded.

4.2.4.3. Determination of Methods for Particle Suspension: The collected particles needed to be suspended in a medium that was suitable for analysis by Coulter (electro-resistance) counting, as well as light microscopy and scanning electron microscopy. In an appropriate suspending medium the particles should not agglomerate. For UHMWPE, this requires an organic medium since the UHMWPE particles are hydrophobic. Metal particles, on the other hand, suspend better in an aqueous medium. Therefore two choices for particle suspension were evaluated. In the first methanol was directly added to the particles. In the second two drops of a dispersant (Coulter IB) was first added to the particles. To keep the polyethylene particles in suspension, two drops of a dispersant
(Coulter type Ib, anionic) were added to each tube of particles. Distilled water was then added to one ml. The particles in either suspending medium were sonicated (Mettler Electronics, Ultrasonic cleaner) for 10 minutes. The two suspending mediums were evaluated for degree of particle agglomeration, and ease of analysis.

4.2.5. Validation of Digestion Protocol: The success of a digestion method for extracting polymer, metal, and possibly other types of particles depends on certifying that the recovered particles truly represent the foreign particulate that was in the tissue. Therefore, several tests were undertaken to examine the validity of the digestion protocol that was developed using concentrated Nitric Acid as the digest agent (based on results from sections 4.2.4.).

4.2.5.1. Effect of Direct Exposure of Nitric Acid on Metal Shavings: A preliminary experiment was set up to determine the effect of concentrated HNO₃ and concentrated HCl on orthopaedic alloys. Metal shavings of Ti6Al4V, stainless steel, and CoCr were obtained by filing these metals while they were turning on a lathe. Because of this method for obtaining the shavings, some iron contamination from the file was inevitable. As much as possible of the iron filings were removed by passing a magnet over the metals. However, some contamination probably still remained. Each of the three metals was placed in the bottoms of 1.5 ml polypropylene tubes. The tubes were filled with the acid and placed in a 70°C oven overnight.
4.2.5.2. Effect of Direct Exposure of Nitric Acid on Metal, Polymer and Ceramic Particles: In a second experiment, powders and beads of Ti, CoCr, and HDPE (Table 4.4) from various companies were exposed to 1 ml concentrated HNO₃ for 48 hours at room temperature. All of the particles were weighed on a microbalance (Mettler AE) before exposure. The 1 µm CPTi was received from Richards already suspended in H₂O, having an unknown concentration. Approximately 8 ml of the suspension was centrifuged, the supernatant drawn off and the particles dried in a 50°C oven for 24 hours before being exposed. The particles were shaken in their tubes several times during the exposure period. At the end of 48 hours, the tubes containing metal particles were centrifuged, the concentrated HNO₃ was drawn off and reserved for graphite furnace Atomic Absorption Spectroscopy (AAS-Perkin Elmer 2380 HGA-400) analysis.

The HDPE particles, alumina particles, and the 1.5 µm Ti particles were collected and suspended in water for SEM, LM and Coulter analysis. Unexposed particles were also analyzed for comparison.

A difficulty was encountered in suspending the 3 µm Astromet Ti particles. These particles constantly clumped together, even after rigorous sonication. A possible reason for this was that:

"Many fine metal powders are manufactured by a grinding process in which a stearate is added to the powder to prevent spontaneous welding of the fine particles to each other as they are being formed. Such a powder is likely to disperse easily in an organic fluid, but will not be wetted by water. Simply rinsing such a powder in an organic solvent is unlikely to completely remove the stearate layer-
Table 4.4. Size of metal, polymer and ceramic beads and powders used to validate the digestion protocol.

<table>
<thead>
<tr>
<th>Material</th>
<th>Form</th>
<th>Supplier</th>
<th>Diam. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F75</td>
<td>Beads</td>
<td>Astromet</td>
<td>420 to 710</td>
</tr>
<tr>
<td>CPTi</td>
<td>Beads</td>
<td>Astromet</td>
<td>500</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>Beads</td>
<td>Astromet</td>
<td>500</td>
</tr>
<tr>
<td>CPTi</td>
<td>Powder</td>
<td>Astromet</td>
<td>1 to 5</td>
</tr>
<tr>
<td>CPTi</td>
<td>Powder</td>
<td>Richards</td>
<td>1.5*</td>
</tr>
<tr>
<td>HDPE</td>
<td>Powder</td>
<td>Richards</td>
<td>2.85*</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Powder</td>
<td>Astromet</td>
<td>0.64</td>
</tr>
</tbody>
</table>

* Determined by Coulter analysis
and it will usually be necessary to use a surface active agent to aid
in dispersion of the powder." (Kaye, 1981)

Many different dispersants were used (Coulter I-III, and glycerol) in
an attempt to suspend the Astromet Ti in H2O, but none worked.
Therefore, SEM, LM and Coulter analysis was performed only with the
Richards Ti particles.

4.2.5.4. Digestion of Control Tissue Spiked with Known Particles:
To validate the entire digestion protocol, control tissue was spiked
with known particles. The particles were then extracted using the
developed digestion protocol. Muscle tissue (grocery store steak)
was cut into four 1 cm³ sections. HDPE particles suspended in MeOH,
Astromet Ti particles and Al₂O₃ particles suspended in distilled
water were injected into the tissue. Since it was impossible to be
sure that all of the particle solution was injected into the tissue,
the concentration of particles in the tissue was unknown. The tissue
was lyophilized and particles extracted. Particles were prepared for
SEM, LM and Coulter analysis (as described in sections 4.7. - 4.10.).
It was discovered later that injection of particles into already
dried tissue was much easier to do. This was how tissue with 1.5 μm
Ti particles (Richards) was prepared.

4.2.5.4. Digestion of Retrieved Tissue: Retrieved synovial tissue
samples (Table 4.1) in all states (unfixed, formalin fixed or
paraffin embedded) was digested using the developed protocol. The
efficacy of the digestion protocol for synovial tissue was
determined. Light microscopy and scanning electron microscopy were used to determine if foreign particles (metal, polymer, carbon, composite) were truly isolated from the tissue. Particle shape, size and composition were also examined with light microscopy, scanning electron microscopy as well as Coulter analysis.

4.2.6. In Vitro Generation of Particles: Particles were generated in vitro using a screw against plate particle generator. This particle generator is similar to the fretter simulator described in ASTM F897, however it has greater power for increased particle production. The generator is connecting rod driven with a variable speed motor (Emerson-Horizon 1).

Both Poly-2 and PEEK composite plates were used in the generator. Poly-2 plates were machined from unimplanted total condylar knees (Zimmer Insall/Burstein). Composite PEEK plates were made from injection molded 30% chopped-carbon-fiber-reinforced bendbars (Dexter composites) by simply cutting the ends and drilling and countersinking the holes. Milling was not necessary. Two-hole plate dimensions to fit the screw/plate particle generator were 2.86 cm (1.125 in) x 1.25 cm (0.492 in) x 0.6 cm (0.236 in). The spacing between the centers of the two holes was 1.59 cm (0.625 in). A 3/16" drill and a 5/16" spherical ballmill were used to drill and countersink the holes. For both the Poly-2 and PEEK plates, titanium alloy screws (A.O.- Ti6Al4V) were used.

The plate and screw set-up fit into a beaker of distilled
filtered H$_2$O. The particle generator was run for 2 weeks and 6 weeks at low speed (between 1 and 2). Two plates of each material were run at each time period.

Composite PEEK particles were collected by centrifuging the water/particle mixture and discarding the supernatant (since PEEK sinks in water). The Poly-2 particles were collected by adding dispersant to the beaker and sonicating for at least 15 minutes to suspend the particles, a sample of particles for analysis was then withdrawn directly from the beaker.

Complications arose when several of the beakers of particle/water mixtures appeared to be contaminated, possibly with bacteria. Because of this, particles were collected, and then exposed to concentrated HNO$_3$ for 24 hours, in an attempt to digest any contamination.

4.2.7. Preparation of Particles for Light Microscope and SEM

Analysis: Before any analysis, the final state of particles which were either extracted from tissue or generated in vitro was in a water suspension. From this suspension, a sample was obtained. To get the particles well suspended and unagglomerated, the particles were sonicated for at least 15 minutes. Shaking the tube first was also helpful. From this suspension, 2-80 µl were withdrawn, depending on the concentration of particles (as indicated by cloudiness). Particles from this suspension were prepared for light microscopy and SEM both with and without the use of filters.
4.2.7.1. Particle Preparation for LM and SEM Without the Use of Filters: An attempt was made to find an alternative for collecting the particles on filters, since particles less than the pore size of the filter are lost. To avoid this, a method for drying the particles directly on microscope slides was pursued. A drop of the water/particles mixture was put on a microscope slide, covered with a petri dish and left to dry. On occasion the particles dried without complication. The more usual occurrence, though, was the presence of crystallites on the slide that precipitated out while drying (these looked like salt crystals). Another option that was tried was mixing the particle/water droplet with a water soluble mounting medium (Permaflour, Lipshaw Immunon). The degree of success with this technique depended on the amount of residual EtOH in the particle suspension. EtOH had a tendency to spread on the slide, and therefore the particles were not contained.

A quick view of the particles was obtained for light microscopy by immediately coverslipping a drop of particle suspension without using any mounting medium. Particles prepared this way, however, would not remain suitable for analysis for more than a few hours due to clumping and drying effects.

The use of either the water soluble mounting medium or the direct coverslipping techniques for preparation of particles for light microscopy were not suitable for SEM. Since 0.05 µm and 0.1 µm filter pore sizes were available, and consistent reliable results
were obtained with the filters, the filters were continued to be used.

4.2.7.2. Particle Preparation for LM and SEM Using Filters. The quantity of particles removed for filtering varied depending on the concentration of debris (as indicated by the blackness or cloudiness of the final suspension), and on the diameter of the filter (13 or 25 mm). Since this was a trial and error process, more than one filter was sometimes used for each sample.

The particles were filtered in one of two ways. In the first method, nitrocellulose filters 13 mm in diameter with 0.1 μm pores (Millipore) were placed in 13 mm stainless steel Swinnex filter holders (Millipore). The Swinnex was attached to a 20 cc syringe. The syringe was filled with 10 cc filtered distilled water. The particle aliquot was added to the water. The particles were collected on the filter and rinsed with another 10 cc of filtered water. The smallest pore size that could be used with this method was 0.1 μm. Even at this size, a great deal of pressure usually needed to be applied to the syringe, and sometimes the filters would break.

In the second filtration method a small vacuum pump (Cole-Parmer Dyna-vac) was attached to a 150 ml filter flask and a 25 mm stainless screen glass filter holder (Millipore). Particles were collected on nitrocellulose filters (Millipore) 25 mm diameter with 0.05 μm pores. The filters were dried, preferably overnight, on
paper towels while covered with a petri dish.

Once the filters were completely dried, they were mounted for SEM or light microscopy. At first, the 0.1 μm filters were used for light microscopy, and the 0.05 μm for SEM. It was soon decided to cut the 25 mm 0.05 μm filters into quarters. One quarter being mounted for SEM, and another quarter processed for light microscopy. The remaining half of the filter was reserved. By cutting samples for LM and SEM from the same filter, it was assured that particles observed with LM were representative of particles observed with SEM. Additionally, this procedure reduced the number of filters required.

4.2.8. Light Microscopy of Filtered Particles: For light microscopy, the filters were mounted and coverslipped with standard mounting media (Eukitt). The nitrocellulose filters became transparent when in contact with the Eukitt (the filters will also clear if in contact with a drop of standard emersion oil). It was noticed several weeks after processing that some of the filters turned opaque. A different mounting media may be required if filters are to retain their transparency for more than a few weeks. One such media is Permount. Filters mounted with this media remained transparent.

Particles were examined with a reflected light microscope (Olympus BH2) which had polarizing capabilities. Particle dimensions could be determined directly with an eyepiece micrometer calibrated with a 1 mm graticule that contained 0.01 mm divisions, or indirectly
by taking micrographs of both the particles and the graticule.

4.2.9. Scanning Electron Microscopy of Filtered Particles: For SEM analysis (JEOL 840), filters were mounted to aluminum stubs with double sided tape. Four filter quarters could be mounted for each large (30 mm diameter) stub. The filters were coated with palladium, which was chosen as the conductive coating for elemental analysis reasons. Palladium only has one peak on the EDXA spectrum compared to gold which has several peaks. Therefore, there is less chance for interference from the palladium coating than from the gold coating when performing elemental analysis.

The filters were found to be quite sensitive to beam damage from the electron microscope. Specific parameters were necessary to give a good image with high resolution and virtually no beam damage. These were 25 KeV, 15 mm working distance, and $6 \times 10^{-12}$ amps of probe current. For EDXA elemental analysis (Tracor Northern 5500), a higher probe current ($3 \times 10^{-10}$ A), and longer working distance (25 mm) was required for elemental detection. This usually damaged the filter. Therefore, pictures of a particle were taken before that particle was analyzed for composition. Since only elements that are heavier than sodium could be determined with this EDXA system, EDXA could not be used to identify polyethylene or carbon.
4.2.10. Coulter Multisizer Analysis

Size distributions of particles were obtained using an electrical resistance particle size analyzer (Coulter Multisizer and Sample Stand II). Particles suspended in water were sonicated for at least 15 minutes. A 40-120 µl aliquot was added to 50 ml Izoton III electrolyte. Once again, the exact amount of particles analyzed depended on the concentration of the sample. For the smaller diameter particles, the 30 µm orifice tube was used in the Coulter sampling stand. Particles down to 0.6 µm were detectable. The sample was stirred in the beaker of electrolyte during analysis. The analysis was run in manometer mode using a 500 µl analytical volume.

4.2.11. Comparison of Particles obtained by Tissue Digestion with Particles Observed in Histological Sections: Tissue originally embedded in paraffin blocks (lab #'s 282, 286, 324, 359 - Table 4.1.) was digested for particle extraction using the protocol resulting from sections 4.2.4. and 4.2.5.. Each of the tissue blocks had accompanying hemotoxylin and eosin stained tissue sections. Using light microscopy, the stained sections were examined for presence or absence of wear debris, for the type of wear debris (birefringent or black) and for the biological response to the wear debris. Polarized light was used with magnifications up to 600x (40x objective). Magnification of 1500x (100x objective) was also used to further identify small particles. Particles extracted from digestion of the
tissue were also examined with light microscopy under the same conditions as the stained tissue sections.

4.2.12. Comparison of Poly-2 Particles Generated In Vivo with Poly-2 Particles Generated In Vitro: To determine if the screw against plate particle generator could be used to generate physiologically relevant particles, particles extracted from retrieved tissue were compared with particles generated in vitro. Poly-2 particles generated in vitro (Section 4.2.6.) were examined with light microscopy as well as SEM and Coulter. Unfixed tissue specimens (lab #’s 248, 282, and 297 - Table 4.1) were digested. Particles extracted were also examined with LM, SEM and Coulter for comparison with the in vitro particles.

4.2.13. Comparison of Poly-2 Particles Generated In Vitro with Composite PEEK Particles Generated In Vitro: Composite PEEK particles and Poly-2 particles generated in vitro (Section 4.2.6.) were compared using both light microscopy, SEM and Coulter.
4.3. Results

4.3.1. Digestion of Tissue for Particle Extraction

4.3.1.1. Comparison of Digest Agents: The results of tissue
digestion by potential digest agents are given in Table 4.5.
Results are given for digestion of 0.2 to 0.3 grams of tissue that
had been first dehydrated. Digestion was considered complete when
all tissue (as observed visibly) had gone into solution. Usually a
clear solution remained with black particles sinking to the bottom of
the tube. Occasionally some particulate could be seen floating on
the surface.

Several disadvantages for using sodium hypochlorite for
digestion were discovered. First, in order for tissue digestion to
be complete, repeated exposures of the tissue to new sodium
hypochlorite was required. This involved centrifugation of the tube,
aspiration of the supernatant and addition of more sodium
hypochlorite. This procedure can result in loss of particles.
Second, under SEM/EDXA analysis, chlorine was found to be present
(McMahon, 1992). Additionally, sodium hypochlorite does not dissolve
hemosiderin (McMahon, 1992). Hemosiderin is an iron rich protein
probably in the form of ferritin (Churchill, 1989). Ferritin is a
protein constituting a storage form of iron in liver and other
tissues. It consists of an outer shell of 24 molecules of a protein
of mass 18.5 KDa surrounding a crystalline region of iron (III),
largely as its hydroxide \( \text{Fe}_2(\text{OH})_3 = \text{rust} \), which may be filled to a
variable extent. When completely filled, the ferritin contains 23%
Table 4.5. Comparison of Digest Agents for Particle Extraction from Joint Tissue. Results in this table are for 0.02-0.03 g dehydrated tissue exposed to 0.5 ml digest agent.

<table>
<thead>
<tr>
<th>Digest Agent</th>
<th>Temp.</th>
<th>Time for Digestion</th>
<th>Hemosiderin dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na Hypochlorite</td>
<td>RT</td>
<td>3X @ 12-18 hrs</td>
<td>no</td>
</tr>
<tr>
<td>2 N NaOH</td>
<td>RT</td>
<td>Undigested*</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>24 hrs</td>
<td>no</td>
</tr>
<tr>
<td>Concentrated HNO₃</td>
<td>RT</td>
<td>24-48 hrs</td>
<td>yes</td>
</tr>
<tr>
<td>35% HNO₃</td>
<td>RT</td>
<td>Undigested**</td>
<td>-</td>
</tr>
<tr>
<td>17% HNO₃</td>
<td>RT</td>
<td>Undigested**</td>
<td>-</td>
</tr>
</tbody>
</table>

* undigested after 1 week
** undigested after 2 weeks
iron (Churchill, 1989). Therefore, hemosiderin is iron present in particulate form. For particle analysis with coulter and SEM the hemosiderin must be removed.

Sodium hydroxide (2 N) was also examined as a potential digest agent for synovial tissue. At room temperature, the base didn't digest the tissue, even after one week. However, 2N NaOH digested the tissue completely within 24 hours if the tube with tissue and NaOH were placed in a 70° C oven. Visibly, the digestion appeared to be complete, and only one digestion was required.

The use of sodium hydroxide for tissue digestion was also found to have limitations. Although the NaOH appeared to work well, this base did not dissolve out hemosiderin. In addition, it has recently been found by another research group (Campbell, 1992) that NaOH reacts with titanium particles by forming a hydroxide. The use of sodium hydroxide for tissue digestion has since been discontinued by this group.

Nitric acid will digest hemosiderin. It was found that digestion of the tissue and removal of hemosiderin could be accomplished in one step (Table 4.5). Within 24 hours, at room temperature, wet tissue was completely digested (as observed visibly). Within 48 hours, at room temperature, dried tissue was completely digested for all volumes of nitric acid. In an attempt to speed up the digestion for the dried tissue, the tissue was first saturated in distilled water before the acid was added. This slowed down the digestion. Lower concentrations of nitric acid (35% and
17%) did not digest dried tissue. These samples remained undigested even after two weeks.

4.3.1.2. Particle collection and Suspension: Based on the previous results, concentrated nitric acid was chosen as the digest agent. In order to extract the particles by centrifugation from the acid/digest solution, the density of the acid was lowered. Neutralizing the acid with a base (as described in the methods section) did allow for the addition of EtOH to lower the density below that of UHMWPE, without causing a reaction. The density was shown to be lowered by the sinking of an UHMWPE shaving from an unimplanted tibial plateau (Insall/Burstein). Although the density was lowered, a salt precipitate, NaNO₃, formed (which probably should have been expected).

The alternative method of diluting concentrated HNO₃ to 17% acid before adding either methanol or ethanol did not cause a reaction. To 0.5 ml concentrated acid, 1 ml distilled water was added. The tube was slightly shaken. Eight ml methanol or ethanol were then added. Adding ethanol or methanol lowered the density of the solution to 0.85 g/cm³, much less than UHMWPE. An UHMWPE shaving sank in this solution.

Two options for resuspension of the extracted particles were considered. The first was to resuspend in methanol, since UHMWPE sinks in methanol, and does not clump. Several disadvantages of methanol were found. First, it was difficult to collect particles by
filtration since the methanol dissolved the filters that would clear in mounting media. Secondly, the use of methanol as the suspending media required that the electrolyte for the Coulter be a methanol/lithium chloride solution. This solution is difficult to keep ultrapure. Finally, dispersing metal particles in methanol, and keeping them suspended for sampling was also found to be difficult. Metal particles quickly sink in methanol due to low density. In addition, metal particles had a tendency to agglomerate in methanol.

The second option for resuspension of extracted particles was to use a dispersant and water. Water is miscible in the prefiltered, aqueous Coulter electrolyte, Isoton III. Water is also easily filtered for particle collection. It was found that the addition of Coulter dispersant IIb allowed for particles extracted from tissue, as well as HDPE powder (Richards) to be suspended in distilled water. It was also seen, with SEM, that Coulter dispersant IIb was not contaminated with any particles.

4.3.1.3. Digest Protocol: Based on the previous results, a stepwise digest protocol was defined. The following is a summary of the digest protocol:

**Step 1.** Freeze dry tissue

**Step 2.** Cut tissue with a razor blade. Weigh out 0.02-0.03 grams on microbalance. Place tissue in 10 ml polystyrene screwcap tube.

**Step 3.** Add 0.5 ml concentrated HNO₃ (70% HNO₃). Digest tissue for 24 to 48 hours (depends on tissue). Tissue is digested when the nitric acid is transparent, usually
yellow. Remaining carbon and metal will sink to the bottom of the tube. Polyethylene will float, but usually there is not enough to notice it on top or clouding the acid.

* If only metal particles (or particles with densities greater than 1.352) are to be collected, skip steps 4 and 5.

Step 4. Add 1.5 ml distilled, filtered water. Gently shake tube.

Step 5. Fill the rest of the tube (approximately 8 ml) with filtered methanol. Using a Pasteur pipette, mix the methanol thoroughly with the diluted acid.

Step 6. Centrifuge the tube for 30 minutes at 2500 RPM.

Step 7. Draw off the supernatant and discard.

Step 8. Add 2 drops dispersant (Coulter type Ib).

Step 9. Add filtered distilled water to make 1 ml solution.

Step 10. Sonicate the tube for 10 minutes.

4.3.2. Validation of the Digest Protocol: The efficacy of using concentrated HNO₃ for digesting tissue without digesting or altering the particles within the tissue was examined. Additionally, the use of this digestion protocol for extraction of particles from retrieved tissue was evaluated.

4.3.2.1. Effect of Direct Exposure of Nitric Acid on Metal Shavings: The results of the metal shavings experiment determining if concentrated HNO₃ of HCl could dissolve orthopaedic alloys are shown in Table 4.6. Nitric acid did not visibly dissolve any of the metals, although all of the solutions turned from white to yellow,
indicating that some reaction had taken place. It was not known if the yellow color was due to some dissolution of the residual iron filings or to the other metals. In contrast, all of the metals dissolved in HCl. Total dissolution of stainless steel turned the acid solution yellow green. The CoCr solution was a blue green color, and the Ti6Al4V solution was a gray black color. Obviously, HNO3 did not affect the metals to the extent that HCl did; however, some reaction did occur as indicated by the yellowing of the acid.

4.3.2.2. Effect of Direct Exposure of Nitric Acid on Metal, Polymer and Ceramic Particles:

AAS Results: A second, more controlled experiment was performed to examine the effects of HNO3 on metal particles. Dissolution results of Ti and CoCr beads and powders exposed to concentrated HNO3 for 48 hours at room temperature as evaluated by AAS are given in Table 4.7. It should be noted that all of the solutions turned a light shade of yellow. In Table 4.7 the original weight of the metals is listed along with the concentration of the metal that was found in solution. It can be seen that all of the metals were dissolved to some extent. The percentage of Ti that went into solution from the CPTi beads and powders was greater for the smaller powders compared to the larger beads. This makes sense since the smaller powders have a larger surface area to volume ratio then the larger beads. Even so, the greatest percentage of dissolution was only 0.51% which was determined for the smallest sized CPTi powder (1.5 μm). This finding
Table 4.6. Color of solutions for metals exposed to concentrated HNO₃ and HCL.

<table>
<thead>
<tr>
<th>Metal</th>
<th>HNO₃</th>
<th>HCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>yellow</td>
<td>yellow green</td>
</tr>
<tr>
<td>Cobalt chromium</td>
<td>yellow</td>
<td>blue green</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>yellow</td>
<td>gray black</td>
</tr>
</tbody>
</table>

Table 4.7. AAS results of metals exposed to 1 ml concentrated HNO₃ for 48 hours. The original size of the metal beads or powder is given along with original weight. The element that was analyzed, and the concentration in µg/ml is also given. In addition, the percent metal that was dissolved and the concentration of dissolved metal in µg/g is listed.

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Original wgt. (g)</th>
<th>Metal AAS</th>
<th>Conc. (µg/ml)</th>
<th>%</th>
<th>µg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>F75</td>
<td>420–710</td>
<td>Cr</td>
<td>1.7</td>
<td>.0024</td>
<td>7.3</td>
</tr>
<tr>
<td>CPTi</td>
<td>500</td>
<td>Ti</td>
<td>196.6</td>
<td>.076</td>
<td>760</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>500</td>
<td>Ti</td>
<td>478.0</td>
<td>.134</td>
<td>1342</td>
</tr>
<tr>
<td>CPTi (Astr.)</td>
<td>3</td>
<td>Ti</td>
<td>147.1</td>
<td>.203</td>
<td>2028</td>
</tr>
<tr>
<td>CPTi (Rich.)</td>
<td>1.5</td>
<td>Ti</td>
<td>88.5</td>
<td>.510</td>
<td>5100</td>
</tr>
</tbody>
</table>
of only 0.51% dissolution for the 1.5 µm CPTi powder is especially significant since a 1.5 µm particle size more closely resembles those particles that may be found clinically. Although the results of this experiment also indicated that Ti6Al4V and CoCr (F75) were affected by HNO₃, smaller sized powders of these materials would have to be obtained to be able to draw more conclusions about the potential fate of these particles in tissue to be digested.

**SEM Results:** Although the AAS results suggested a low dissolution rate for Ti powders exposed to HNO₃ for 48 hours, it was also necessary to determine if the particles were altered morphologically or if submicron particles were preferentially dissolved. These issues were also pertinent for exposure of polyethylene and alumina to HNO₃. Powders of (1.5 µm, Richards), HDPE (2.85 µm, Richards) and alumina (0.64 µm, Astromet) were examined with SEM before and after direct exposure to HNO₃.

In Figure 4.1a, an SEM micrograph shows the as-received CPTi powder. The original state of the particles were generally cuboidal to spherical with rough surfaces. Very small particles, down to 0.1 µm were observed. In comparison, CPTi particles are shown in Figure 4.1b after 48 hours exposure to HNO₃ at room temperature. After direct exposure, the particle morphology did not appear to change. Importantly, small 0.1 µm particles were still found.

Similar results were observed for the as-received HDPE as seen in Figure 4.2a. HDPE particles were larger than the Ti particles. These particles were also rounder and not as jagged as the Ti
Figure 4.1a. SEM micrograph of as-received Ti particles (Richards).

Figure 4.1b. SEM micrograph of Ti particles after exposure to concentrated HNO₃ for 48 hours at room temperature.
Figure 4.2a. SEM micrograph of as-received HDPE particles (Richards).

Figure 4.2b. SEM micrograph of HDPE particles after exposure to concentrated HNO₃ for 48 hours at room temperature.
particles, although the surfaces were rough. Differences were not
apparent upon comparing the as-received particles with the exposed
particles (Figure 4.2b).

Coulter Analysis: The size distributions of the same particles
viewed with SEM were determined using the Coulter fit with a 30 μm
orifice tube. Results are given in Table 4.8. The average particle
size of the Ti particles directly exposed to HNO₃ (1.397 μm)
decreased by 5% compared to the size of the as-received particles
(1.481 μm). The shape of the distribution curves were similar,
however, as well as the size ranges. A 5% decrease in average size
was also found for the HDPE particles directly exposed to HNO₃ (2.694
μm) compared to the average size of the as-received HDPE (2.850 μm).
The size ranges and the shape of the distribution were also similar.
These results can be compared with that found for alumina. A 2%
decrease in average size was determined for the exposed Al₂O₃
particles (0.923 μm) compared with the as-received Al₂O₃ (0.944 μm).
Although small decreases in average particle size were found for both
the Ti and HDPE particles, these were comparable to the decrease
found with the Al₂O₃ particles which should not be affected
chemically by nitric acid.

Based on the results from AAS, SEM and Coulter analysis, it can
be concluded that the effect of 48 hour exposure to concentrated HNO₃
at room temperature is minimal for the HDPE (Richards) and CPTi
(Richards) powders. Although conclusions can not be reached about
the effect of HNO₃ on other orthopaedic alloys and polymers, there is
Table 4.8. Coulter analysis of Ti, HDPE and Al₂O₃ particles before and after digestion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Count</th>
<th>Ave. Diam. (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>205,019</td>
<td>1.481 (.878)</td>
</tr>
<tr>
<td>Ti + HNO₃</td>
<td>92,423</td>
<td>1.397 (.822)</td>
</tr>
<tr>
<td>Ti digest</td>
<td>162,069</td>
<td>1.437 (.892)</td>
</tr>
<tr>
<td>HDPE</td>
<td>52,894</td>
<td>2.850 (.998)</td>
</tr>
<tr>
<td>HDPE + HNO₃</td>
<td>178,037</td>
<td>2.694 (1.071)</td>
</tr>
<tr>
<td>HDPE Digest</td>
<td>319,101</td>
<td>0.944 (.223)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>293,409</td>
<td>0.923 (.225)</td>
</tr>
<tr>
<td>Al₂O₃ + HNO₃</td>
<td>215,351</td>
<td>1.048 (.391)</td>
</tr>
<tr>
<td>Al₂O₃ digest</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
sufficient evidence to warrant the use of nitric acid as the digest agent to extract foreign particles from tissue.

4.3.2.3. Digestion of Control Tissue Spiked with Known Particles: Ti and Al$_2$O$_3$ particles digested out of control tissue were collected without the addition of the water and EtOH since they sunk in HNO$_3$. In contrast, HDPE particles were extracted using the entire protocol. Under SEM, Ti, HDPE and Alumina particles extracted from digestion resembled the as-received particles. An undigested residue was also observed with the HDPE particles, but it did not interfere with SEM observations of the HDPE particles. The residue that was seen with the digestion of the HDPE spiked tissue was not found with the Al$_2$O$_3$ or Ti extracted particles.

The residue associated with the HDPE particles, which were extracted by following the entire digestion protocol, made it difficult to analyze the HDPE digest on the Coulter because the orifice clogged quickly. Therefore, only Al$_2$O$_3$ and Ti digested spiked tissue were analyzed. A 3% decrease was observed for the particles extracted by digestion compared to the as-received particles (Table 4.8). However, a 10% increase in particle size was found for Al$_2$O$_3$ particles digested out of tissue (Table 4.8). This may have been due to agglomeration of the particles.

4.3.2.4. Digestion of Tissue Retrieved from Patients with Poly-2 Implants: It was previously mentioned that the tissue spiked with
Poly-2 did not digest completely whereas the tissue with the Ti and Al₂O₃ particles did. It was found that the addition of the water to dilute the acid, and the methanol to lower the density seemed to cause a reprecipitation of something that had previously been in solution. Since the digestion of the tissue with the Ti and Al₂O₃ particles did not include the water and EtOH steps, this precipitate was not seen. It was soon noticed however with the digestion of retrieved tissue using the entire digestion protocol, that the formation of this precipitate did not always occur.

A possible correlation was noticed between the original state of the tissue and the presence of undigested material. As shown in Table 4.9, the residue was absent for all of the samples that were originally unfixed before digestion. However, as illustrated in the SEM micrograph in Figure 4.3, a spindly residue was found on the filters of those samples that were formalin-fixed before digestion. The filters made from the samples that were originally embedded in paraffin (which also implies formalin fixation) seemed to be coated with this residue as well. This residue could also be observed on filters mounted for light microscopy (Figure 4.4). Although an apparent correlation exists, it was observed that the residue was not noticed with light microscopy for the paraffin embedded sample #282.

From the formalin and paraffin embedded samples, some information about the extracted particles was still obtained. Principally, the larger particles, such as carbon fibers, were readily visible. Unfortunately, it was difficult to acquire size
Table 4.9. SEM and light microscope analysis of particles extracted from digested tissue to determine if an undigested residue was found with the particles. Yes: residue was seen, No: residue was not seen.

<table>
<thead>
<tr>
<th>State of Tissue</th>
<th>Lab #</th>
<th>SEM</th>
<th>LM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfixed</td>
<td>248</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>282</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>297</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Formalin</td>
<td>286</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>324</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>359</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>Paraffin</td>
<td>282</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>324</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>359</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>
Figure 4.3. SEM micrograph of an unknown residue observed after digestion and collection of particles from retrieved tissue (#286-formalin fixed).
Figure 4.4. Light micrograph of an unknown residue observed after digestion and collection of particles from retrieved tissue (#359-formalin fixed).
distributions from the Coulter because of clogging.

Particles extracted from the frozen samples were examined with both SEM and LM. It was immediately evident that a wide size distribution existed from submicron particles to particles of several hundreds of microns. The morphology of the particles also varied greatly. To get an accurate size distribution, multiple filtrations may be necessary instead of just the one filtration collecting all particles greater than 0.05 μm.

Shown in Figure 4.5 are particles collected from sample #282. The patient that this sample came from had a titanium femoral component and titanium backed Poly-2 patella and tibial component. Using EDXA, several sizes of particles were identified as Ti which are shown in Figure 4.5a. Notice that although the 10 μm particle at the bottom right of the screen appears to have much higher contrast than the 5 μm particle at the upper left, they were both identified as Ti. Even the small 1 μm particle was identified as Ti. The EDXA spectrum of these particles was taken for approximately 100 seconds. To use EDXA simply for identification and not for quantitative analysis (such as determining exact composition) an acquisition time of 100 seconds, or even fewer seconds is acceptable. The large 100 μm particle in Figure 4.5b. was not determined to be Ti, although Ti was found on its surface. It is suspected that this particle is UHMWPE, although this cannot be confirmed.

Particles extracted from digestion of sample #282 were also examined with light microscopy. An advantage of light microscopy is
Figure 4.5a. SEM micrograph of particles collected from digestion of retrieved tissue (#262-unfixed). The arrows point to three particles identified as Ti using EDXA.

Figure 4.5b. SEM micrograph of a large 100 μm particle extracted from digestion of retrieved tissue (#262-unfixed). This particle was not identified as metal, however, Ti was found on its surface.
that birefringence of polyethylene is readily visible. In Figure 4.6 several particles appear bright white. Once again, there is no direct proof that these particles are polyethylene. Distinguishing between carbon and metal debris with light microscopy is also practically impossible, unless the carbon retains its shape in fiber form which is seen in Figure 4.6 as well.

From the previous discussion it was demonstrated that particles could be collected from retrieved tissue using the nitric acid digestion protocol. Identification of the particles as carbon, UHMWPE, or metal was difficult but some progress was made if both light microscopy and SEM were used together. To examine smaller particles, it was necessary to look at particles that were collected without the background residue that was found with several of the digested tissues. Therefore, particles retrieved from digestion can be used as long as the results are tempered with an understanding of the limitations of the digestion protocol and analysis techniques.

4.3.3. Limitations of Coulter Analysis and SEM Analysis for Particle Analysis: Both Coulter and SEM analysis have their advantages and disadvantages for analyzing the size of particles digested from tissue. For both of these methods to be useful, particles must be well sonicated before analysis. The importance of sonicating the particle suspensions for at least 15 minutes and analyzing the particles immediately after sonication is illustrated in Figure 4.7. In Figure 4.7a the size distribution for the as-received alumina
Figure 4.6. Light micrograph of particles extracted from digestion of a fresh-frozen tissue (#282).
particles are compared with alumina particles exposed to HNO₃. It appears as if the exposed particles are actually bigger than the as-received particles. However, because of clogging of the orifice, several minutes elapsed before a good count of the Al₂O₃ particles was obtained. When a new distribution of the exposed particles was acquired immediately after sonication, the results were very different. As seen in Figure 4.7b, the two curves overlapped. Apparently the exposed alumina particles represented in the first distribution had reagglomerated or clumped before analysis.

Even with well sonicated particles, both Coulter and SEM have their limitations in determining size and shape of particles. Since 0.6 μm is the lower limit for detection by the 30 μm orifice tube on the Coulter, particle suspensions that contain a significant fraction of particles less than 0.6 μm may be misrepresented by Coulter analysis. This was illustrated in the previous results analyzing the Al₂O₃ (Astromet) particles. The average size for the alumina particles was found to be 0.944 μm (Table 4.6). This is 30% greater than the particle size (0.64) reported by Astromet. In addition, the size distributions for the Richards Ti particles (1.481 ± 0.878) and the Richards HDPE particles (2.850 ± 0.998) were found to be different by another laboratory analyzing these same particles with Coulter (Campbell, 1992). Results from this laboratory using a 20 μm orifice tube (compared to the 30 μm tube used in this study), indicated a particle size of 0.7 μm ± 0.44 for the Ti particles and 1.765 ± 0.825 for the HDPE particles. This suggests that Coulter
Figure 4.7. Comparison of size distributions of as-received Al₂O₃ particles (Astromet) with Al₂O₃ particles exposed to HNO₃ for 48 hours. Clumping of the exposed particles caused the distribution to be shifted to the right and to flatten out (a). After thorough sonication, the distributions for both particle types overlapped (b).
analysis may not be accurate for particle distributions with significant submicron fractions.

Another problem that is encountered with Coulter analysis is the assumption of sphericity in determining particle diameter. Since very large numbers of particles are being sized, it is assumed that largely non-spherical particles will be compensated for by the effects of averaging. This works well for fairly uniform particle distributions. For non-uniform distributions with many non-spherically shaped particles of many sizes, the averaging effect may not work.

To examine this, Ti particles analyzed on the Coulter were also sized with SEM. The results are shown in Table 4.10. Number indicates the actual number of particles that were analyzed. It can be seen that the average diameter of the Ti particles according to SEM was 30% less than that determined by Coulter. The shape factor, which describes how close to spherical the particles are is also greater than 1 (which is the shape factor for a sphere). In addition to Ti particles, particles digested from a tissue sample from a patient with a Poly-2 implant was also sized with both Coulter and SEM. Once again the average diameter of the particles according to SEM was less (by 30 %) than that determined by Coulter. In fact, the size of the particles were smaller than Coulter could detect. The shape factor of 2.2 also indicated that many particles deviated from sphericity.
Table 4.10. Results comparing average diameters of Ti powder and extracted particles using Coulter analysis and SEM analysis. Number is the actual number of particles that were analyzed. The shape factor is assumed to be one in Coulter analysis since this is the shape factor for a sphere. For SEM analysis, the shape factor was determined by the ratio of the maximum diameter divided by the minimum diameter of the particle.

<table>
<thead>
<tr>
<th></th>
<th>Number</th>
<th>Avg. Diam. (μm)</th>
<th>Shape Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/Coulter</td>
<td>205,019</td>
<td>1.481 (.878)</td>
<td>1.000</td>
</tr>
<tr>
<td>Ti/SEM</td>
<td>39</td>
<td>1.080 (.572)</td>
<td>1.425</td>
</tr>
<tr>
<td>P2(#282)/Coulter</td>
<td>59,225</td>
<td>1.252 (.497)</td>
<td>1.000</td>
</tr>
<tr>
<td>P2(#283)/SEM</td>
<td>44</td>
<td>0.403 (.203)</td>
<td>2.189</td>
</tr>
</tbody>
</table>
Evaluating these results is difficult. Although particle size as determined from SEM was smaller than that determined by Coulter, only 39 and 44 particles from one field of view was examined with the SEM, compared to the thousands of particles counted by Coulter. Determining fields of view and magnification for SEM analysis can also bias results. Complete particle characterization with the SEM would necessarily include many fields of view at various magnifications. Size distributions determined by Coulter analysis must be evaluated with consideration of how uniform the particle distribution is and whether or not a significant fraction of particles is below the detection limit of the Coulter.

It was considered beyond the scope of this project to do a comprehensive analysis of size and shape for the particles digested from tissue and generated in vitro. Instead, general morphological features and sizes were evaluated.

4.3.4. Comparison of Particles Observed in Histology Slides with Particles Collected from Tissue Digestion: Tissue embedded in paraffin, and slides from these blocks stained with H&E were obtained for four patients that had received implants containing Poly-2. The biological response to the wear debris present for the four cases was similar to that reported in the literature and is listed in Table 4.11. Generally, various amounts of debris were observed, usually associated with a giant cell response. In two of these cases, debris was found in very acellular tissue. Identifiable carbon fibers were
Table 4.11. Light microscope examination of tissue from patients that had received Poly-2 implants. Slides were taken from paraffin blocks that were subsequently digested.

<table>
<thead>
<tr>
<th>Patient #</th>
<th>Biological Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>282</td>
<td>Florid giant cell reaction, a great amount of UHMWPE both large and small, and black debris present</td>
</tr>
<tr>
<td>286</td>
<td>Very vascularized, many PMNs present, not much black debris present, much more UHMWPE in necrotic looking tissue</td>
</tr>
<tr>
<td>324</td>
<td>Particles in very acellular tissue, mostly black debris, very little birefringent material</td>
</tr>
<tr>
<td>359</td>
<td>Very vascularized tissue, similar to #286, giant cells present, pmns evident, moderate amount of black debris, not much UHMWPE</td>
</tr>
</tbody>
</table>
dispersed throughout all four cases.

An example of debris from sample #282, which has been engulfed by a giant cell, is shown in Figure 4.8a. Both UHMWPE particles and black (metal or carbon particles) are present. The size of the polyethylene particles are approximately 10 and 20 μm. The sizes of the black particles are all less than 5 μm, and many were much less. Measuring these particles is difficult, even more so when a large amount of the black debris is packed into one giant cell as illustrated in Figure 4.8b.

These particles can be compared to those in Figure 4.6. Notice that the digested particles are spread out on the filter so that they can be easily counted and sized (if at a higher magnification). The general characteristics of the black debris that was collected after digestion and the black debris present in the histology slides are very similar. However, at the magnification of light microscopy, the detailed morphology cannot be observed. Examination of the collected particles the light micrographs reveals that the debris that was collected through digestion of tissue is similar to the debris observed in stained tissue sections.

Although black particles (which are indicative of either carbon or metal debris), birefringent particles (most likely being UHMWPE), and individual carbon fibers have been observed in both histological sections and retrieved particles, it was interesting to observe that evidence of composite particles was slim. On occasion, a particle that appeared to be a piece of composite that included both carbon
Figure 4.8a. Light micrograph of tissue surrounding a Poly-2 implant (#282). The giant cell contains distinguishable polyethylene and black debris.

Figure 4.8b. Light micrograph of another giant cell from the same tissue (#282). Because the giant cell contains so much black debris, individual particles can not be distinguished.
fibers and UHMWPE was found, but this was very rare. This may be due to the poor bonding between the UHMWPE and the carbon fibers, or it may be a function of the type of wear situation, or it may be a combination of both composite properties and type of wear. This was an issue that needed to be examined with the in vitro generation of particles.

4.3.5. Particles Generated In Vitro compared with Particles Generated In Vivo: Particles generated with the particle generator using titanium screws and plates made from Poly-2 are illustrated in Figure 4.9. Notice that carbon fibers are bare and that there are many small black particles that could either be carbon or metal. There were very few composite particles present. Birefringent particles were also present in abundance (although not shown in Figure 4.9). Comparing this micrograph with Figure 4.5, it appears that the particles generated in vitro were at least similar to the particles generated in vivo. The particles were usually round or oval shaped with rough edges and many of them appeared flat. Upon looking at the in vitro particles with SEM (Figure 4.10), it was evident that there was some contamination in the particle suspension. This was indicated by the underlying film on the filter and the rod like particles (possibly bacteria). Also notice in this micrograph that the carbon fiber is quite bare of matrix. After exposure of the in vitro particles to concentrated nitric acid in an attempt to eliminate the contamination, particles similar to those shown in
Figure 4.9. a) Light micrograph of particles generated in vitro using Poly-2 plates and Ti screws. b) Light micrograph of particles generated in vitro using CFRPEEK plates and Ti screws.
Figure 4.10. SEM micrograph of particles generated in vitro using Poly-2 plates and Ti screws. A background film is observed covering the filter. Also evident are small rods which may be bacteria.

Figure 4.11. SEM micrograph of the same type of particles in Figure 4.10 that were exposed to concentrated HNO₃ for 24 hours to remove the contamination.
Figure 4.11 were observed.

The size of these particles ranged from submicron to hundreds of microns, although particles 10 μm and less were most unusual. These particles had roughly the same characteristics as the particles observed in Figure 4.5a (particles digested from tissue), however the in vitro generated particles appeared slightly more regular in morphology and the size distribution appeared to be tighter. A more thorough investigation including more fields of view is necessary to draw more definite conclusions.

4.3.6. Poly-2 Particles Generated In Vitro Compared with 30%CFRPEEK Particles Generated In Vitro: Composite PEEK particles that were generated in vitro were also slightly contaminated. However, examination with light microscopy indicated an abundance of black particulate, carbon fibers, and birefringent material (Figure 4.9b). There was also slightly more indication that composite particles as well as individual components were generated as well. In contrast to the bare Poly-2 fibers, several coated carbon fibers were observed with SEM. Similar to the Poly-2 composite was the generation of particles that ranged from submicron to hundreds of microns. In addition, the particles were generally symmetrical, some of them appearing flat.
4.4. Discussion

The identification of polymer particles (particularly UHMWPE) in contributing to osteolysis requires a careful evaluation of the wear products of any potential orthopaedic device which contains polymeric material. This includes polymer composites. In this study, particles that were associated with the wear of orthopaedic implants, which used Poly-2 as a bearing surface, were examined.

In order to examine these particles, retrieved tissue from patients which had Poly-2 implants was digested, and the particles were extracted. An issue of considerable importance was insuring that the particles that were eventually analyzed were not modified or dissolved by the digestion technique. Other studies have reported results from examination of particles that were recovered from digestion processes, however, information is lacking on the validation of their methods. For instance, both potassium hydroxide (Kossovsky et al., 1991, 1992) and sodium hydroxide (Campbell, 1992) have been used as digest agents. Particles recovered have subsequently been sized by photon correlation spectroscopy. Exactly what these particles were is not known. A possibility exists that many of the particles counted could have been hemosiderin particles rather than actual wear particles (Bauer, 1992). Another digestion technique for extracting particles has used a commercial tissue solubilizer, Soluene (Lee et al., 1992). Soluene is a very strong base consisting of toluene and quaternary ammonium hydroxide, plus a small volume of methanol (Packard Chemicals). Soluene was used only
for collection of metal particles and not UHMWPE. Even so, the authors have stated that metal is "relatively insoluble in it" without offering any other experimental evidence.

From experience with using the digestion protocol presented in this study, issues such as overdigestion which can result in the dissolution of metal, and suspension of polyethylene have been carefully examined. The ideal digestion protocol, however, has not yet been attained. Problems exist with digestion of various forms of tissue (such as unfixed vs. fixed vs. paraffin-embedded). How many particles are lost by the digestion process is also not yet known. Nevertheless, progress has been made. Particles that have been identified as metal, polymer, and carbon have been extracted.

This alludes to another important issue, global identification of particles. Particles observed in both histological sections and digestion extractions, generally include metal, polymer and carbon. Often several different metals (Ti and CoCr) could be present. With the development of improved polymers and composites, the future possibility exists that several different polymers and even several different types of reinforcement in composites may be used in the same implant system. Identifying the various particles is difficult. To identify metal particles in thin sections, EDX/A has been used for particles greater than 0.2 μm (Jacobs et al., 1992). For smaller particles, analytical electron microscopy (AEM), in conjunction with an electron energy loss spectrometer (EELS) was employed (Jacobs et al., 1992). This research group also successfully used fourier
transform infrared spectroscopy (FTIR) to identify UHMWPE particles greater than 10 μm. Confirming the identity of particles smaller than this as polyethylene has been difficult with spectroscopy. Another method of doing this is by using a special stain. It was determined that a modified Oil red O stain could be used to identify polyethylene in conjunction with polarized light (Peters et al., 1992, Campbell et al., 1992). Polarizable particles less than 5 μm were identified with this stain. There are limits to the use of this stain since magnification and resolution greater than that afforded by the light microscope is needed to get morphological detail from tiny polyethylene particles.

Other possibilities for particle identification, primarily for those particles that have been isolated by digestion, include using physical properties to separate the particles. Shown in this study was the potential for dissolving the metal and retaining the polymer and carbon particles. Another method which has been attempted is a density gradient (Campbell et al., 1992). Accurate identification of particles is not a simple matter. More work is required to make this feasible.

Methods to study particles have included examining particles generated in vitro. UHMWPE articles have been made by cryogenic attrition (Leigh et al., 1992). Metal powders have been produced specifically for biocompatibility testing by a rubbing/grinding process (Buchhorn et al., 1992). In this study metal and Poly-2 particles generated in vivo were compared with particles that were
generated by the wear of screws against a plate. The particulate debris was grossly compared. It appears that the screw against plate particle generator can produce physiologically relevant particles. More detailed work is required to confirm this. The possibility of comparing various composite materials based on particle characteristics was also demonstrated by the differences and similarities observed between the 30%CFRPEEK composite and the Poly-2 composite.

This study has concentrated on retrieving particles from digestion and comparing them with particles seen in histological sections, and with particles that have been generated in vitro. The motivation for this was the long-term goal of predicting how particles generated from the wear of composites may be tolerated in vivo. The Poly-2 composite particles extracted from digestion in this study were generally characterized. There is also a need for close scrutiny of these particles as well as particles generated in vitro.

It has been demonstrated that macrophages stimulate bone resorption when they phagocytize particles (Murray and Rushton, 1990). Therefore, questions arise such as what are the properties of the particles that make them phagocytizable? Size, surface properties, shape, chemical composition? It has been suggested that any undigestible particle will evoke a macrophage/giant cell response, regardless of the particle type (Boss et al., 1992). However, it can not be ignored that various histiological responses
are observed to carbon particles (Helbing et al., 1980), compared to Teflon particles (Malizia et al., 1984), compared to UHMWPE particles. Phagocytosed particles stimulate increased macrophage proliferation and affect the synthesis of lysosomal enzymes, prostaglandin E₂, cytokines and other substances capable of bone resorption (Goodman et al., 1992). It seems reasonable, that by investigating wear particles to understand particle/host interactions, much will be learned about choosing new composite materials for orthopaedic applications.
5. Summary

Miniflexbars were cut from injection-molded CFRPEEK bendbars. Variation in flexural properties of these MFBs were shown to correlate with variations in local microstructure within the intact bendbar. An overall decrease in flexural strength was found for the MFBs when compared with the flexural strength of the intact bendbar. This could be explained by microstructural differences in fiber orientation and distribution. Therefore, it was concluded that for the 1 x 5 x 30 mm MFBs a "size effect" was not apparent. It was also found that residual stresses were released when the MFBs were cut from the intact bar.

The flexural properties of MFBs were also determined for Ultracek freeform composites. The vast microstructural inhomogeneity of these composites was evident in the variation in flexural strength, strain and modulus for individual MFBs cut from multiple positions in the composite. In addition, the influence of specimen dimensions on flexural testing results was shown to be significant for this composite.

The use of MFBs in mechanical testing to evaluate flexural properties for injection-molded and freeform composites was shown to be advantageous. The small size of the MFBs emphasized the effect of local microstructural differences on mechanical properties. A small size is also beneficial for environmental exposure experiments both in vivo and in vitro. Therefore, MFBs were used to examine the effects of serum on flexural properties of various composites.
Injection-molded CFRPEEK MFBs, continuous fiber reinforced PEEK MFBs, and injection molded CFRPSU MFBs were exposed to 10% serum for 36 weeks at 37°C. It was shown that those MFBs that contained more matrix material and more fiber ends preferentially absorbed more serum solution. However, this did not alter flexural properties. Flexural properties of the PEEK composite MFBs did not change after 36 weeks exposure, regardless of location or orientation. Results from flexural testing the CFRPSU MFBs exposed to serum solution exhibited an increase in flexural strength and modulus and decrease in strain. This was in part attributed to the discovery of pores within the CFRPSU material.

In conjunction with evaluation of composite degradation due to exposure to serum in vitro using MFBs, degradation products recovered from composite wear generated in vivo and in vitro were also evaluated. First, a digestion protocol using concentrated HNO₃ as the digest agent was developed. The effect of concentrated HNO₃ on CPTi and HDPE powders was found to be negligible. The digest protocol worked well for unfixed tissue, however for tissue fixed in formalin and in paraffin blocks, a residual precipitate formed. The protocol needs to be modified to digest fixed tissue.

Determining sizes of digested particles with both SEM and Coulter was found to have limitations. Nonetheless, submicron particles to particles hundreds of microns in size were found from digested tissue, as well as from in vitro generation. Global comparison of Poly-2 particles retrieved from digestion compared to
particles seen in histological sections indicated similarities. The advantages of extracting particles from tissue for characterization were evident.

Poly-2 particles generated in vitro using a screw-against-plate particle generator were similar to those particles digested from tissue. Particles were also recovered from the wear of composite PEEK plates and titanium screws. Although future work is necessary to optimize this in vitro method for generation of particles, it was shown that this method can produce physiologically relevant particles.
LITERATURE CITED


Bauer T.W., personal communication (1992)


Blundell D.J., "On the Interpretation of Multiple Melting Peaks in Poly(etheretherketone)," *Polymer, 28*, pp. 2249-2251 (1987)


Churchill's Illustrated Medical Dictionary, Churchill.Livingstone, 1989


Dexter Corporation, Composites Division, Cleveland, Ohio, Material Data Sheet (1989)


ICI Advanced Materials, Wilmington, Delaware, Material Data Sheet (1986)

Ishida H., Polymer Composite Processing - Class Notes, Department of Macromolecular Science, Case Western Reserve University (1988)


Kwarteng K., Stark C., SAMPE Quarterly, October (1990)


McMahon J.T., personal communication, 1992


Meunier A., personal communication, 1992


More N., Baquey C., Barthe X., Rouais F., Rivel J., Biocompatibility of Carbon-Carbon Materials: in vivo study of their Erosion Using Carbon Labelled Samples,


Packard Instrument Company, Meriden, CT, Material Data Sheet (1990)


