PROCESSING AND CHARACTERIZATION OF NANOPARTICLE AND CARBON NANOTUBE REINFORCED CONTINUOUS FIBER CERAMIC NANOCOMPOSITES BY PRECERAMIC POLYMER PYROLYSIS

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_________________________  THESIS COMMITTEE
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In this work, two types of Continuous Fiber Ceramic Composites (CFCCs) were manufactured using preceramic polymer pyrolysis (PIP) method for mechanical testing. Nicalon™ ceramic grade silicon carbide fiber was used as the reinforcements, and KiON CERASET® preceramic polymer was used as the matrix in this study. Further, the effects of nanoparticles, carbon nanotubes, and the combination of the two, as CFCC reinforcements, compared to their base CFCCs on processing and flexural mechanical performance of Nicalon/KiON CERASET® CFCCs by PIP method have been investigated. Nicalon™ ceramic fiber was used as the primary fabric for all four types of CFCCs in this work. KiON CERASET® preceramic polymer was mixed with nano size fillers in the presence of a surfactant agent to give a good dispersion of the particles and was used as the nano-matrix. Initial work from nanoparticle reinforced CFCCs led to further investigations on the effects of using carbon nanotubes, as well as their use in conjunction with nanoparticles, on mechanical performance of continuous fiber ceramic nanocomposites. Yttrium oxide nanoparticles with an average size of 27 nm were used as the inclusion with weight percentage of 15%. Carbon nanotubes were grown directly on the surface of Nicalon™ fabric via in-house chemical vapor deposition process. Characterization analysis and dispersion studies of the samples using scanning electron microscopy were conducted. Four-point bending test was also conducted to evaluate the flexural mechanical performance of the ceramic nanocomposites samples at room temperature. Combination of nanoparticle and carbon nanotube reinforced CFCCs, consistently showed significant improvement in flexural strength and toughness compared to their counterparts without nanomaterial reinforcement or with only one type of nano-reinforcement.
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CHAPTER 1

INTRODUCTION

Ceramic materials have various advantages over metallic materials and their alloys for high temperature applications. These applications in aerospace fields include rocket exhaust nozzles, heat shields and aeronautic jet engine components [1]. Structural ceramics and composites have applications in areas including energy generation, environment, space, transportation and microelectronics [2]. Long-term mechanical reliability is a key issue in their ultimate use for a specific application. The future opportunities for the use of advanced ceramics and various types of ceramic matrix composites in aerospace applications include DoD related applications in aircraft, missiles and spacecraft, and civilian applications in aircraft and space vehicles [3]. This is due to ceramic’s lower density, high temperature strength, and corrosion and oxidation resistance capabilities of the ceramic matrix composites [3]. Traditional monolithic ceramics meet most of the requirements for these applications; however, due to their brittle nature and lack of toughness, they cannot be used as the ideal material of choice. Reinforcement of ceramic materials is a promising method for their toughness improvement. Polymer matrix composites (PMCs) currently account for most of the composite materials used in the gas turbine, despite their relatively low temperature capability of typically less than 150°C [4]. Metal matrix composites (MMCs) are attractive for application at intermediate temperatures while ceramic matrix composites (CMCs) offer exciting possibilities for very high temperature applications where loads are modest [5]. Ceramic Matrix Composites (CMCs) combine reinforcing ceramic phases
with a ceramic matrix to create materials with new and superior properties. In ceramic matrix composites, the primary goal of the ceramic reinforcement is to provide toughness to an otherwise brittle ceramic matrix. CMCs are being developed for applications that require light-weight structural materials, oxidation resistance, and high temperature resistance capabilities including high strength and modulus [1-3]. Fillers can also be added to the ceramic matrix during processing to enhance characteristics such as electrical conductivity, thermal conductivity, thermal expansion, hardness, etc. The combination of these characteristics makes ceramic matrix composites attractive alternatives to traditional industrial materials such as high alloy steels and refractory metals. An important type of ceramic matrix composite that is currently being investigated is the Continuous Fiber-reinforced Ceramic Composite (CFCC). CMCs and particularly CFCCs have attracted immense attention for use as high-temperature structural materials [5-9]. CFCCs are significantly tougher and more damage tolerant than their monolithic counterparts. These composites are attractive alternatives to monolithic ceramics and whisker-fiber CMCs [6], since CFCCs fail with a tough, high strain mode, whereas conventional ceramics fail with a rather brittle mode [7]. It is the fiber reinforcement in the ceramic matrix that prevents catastrophic brittle failure, by providing various energy dissipation processes during the crack propagation in the matrix as see in Figure1.1.
In both the aerospace and automotive industry, there is an increasing demand for tough, strong, and light weight materials to replace metals and their alloys as structural materials. Future applications such as energy-efficient heat engines and high-subsonic supersonic airplane and spacecraft will utilize high-performance structural materials in selected elevated-temperature areas. The performance of fiber reinforced ceramics remains unchallenged by other materials in the temperature regime above 1200 °C, as shown in Figure 1.2. The use of a CFCC takes advantage of high strength and stiffness to weight ratios combined with the flexibility in tailoring the structure to meet the loading conditions resulting in greatly increased structural efficiency at very high temperatures. These enhanced properties in fiber reinforced ceramic composites (CFCCs) coupled with the utilization of nanotechnology provides a broad research area in processing and performance enhancement of CFCCs reinforced with nanoparticles and carbon nanotubes.
The preceramic polymer pyrolysis route to ceramic chemistry has attracted much attention as it offers a promising and cost-effective way to manufacture CMCs/CFCCs with little to no final machining [10-15] and parts with greater compositional homogeneity [16-18]. Preceramic polymers are organo-metallic polymers which, after curing, are chemically transformed during their pyrolysis step to yield a contributing ceramic phase(s) in the final ceramic part. Other advantages of using the polymer pyrolysis technique include the potential for high reproducibility of ceramic materials with respect to chemical properties and physical characteristics, lower processing temperatures and pressures, and improvement in the CMCs processing technique, including faster thermal cycles, lower rejects, and high reliability of parts. Traditional manufacturing techniques for CMCs (such as Chemical Vapor Deposition/Infiltration (CVD/CVI), powder processing, Sol-gel processing, etc.) are time consuming and are in the order of two weeks [19-21]. Homogeneous parts with complex geometries cannot be manufactured by traditional methods due to the development of large density gradients within the CMCs leading to non-uniform parts [20-21]. On the other hand, the
disadvantage of the polymer pyrolysis technique is the inherent excessive matrix shrinkage [22-26] resulting in large residual stresses and micro-cracks. However, the percentage of the voids and micro cracks due to the pyrolysis can be reduced by successive reinfiltaration/pyrolysis cycles. Other major disadvantage faced in processing CFCCs using Polymer Impregnation Pyrolysis (PIP) process is the amount of processing time it takes to attain the final good quality part. It was demonstrated that by adding different types of micron-sized inactive fillers, the amount of time required to manufacture CFCC samples can be considerably reduced [27]. However, samples manufactured by adding micron-sized inactive fillers, while reducing the processing time, considerably reduced the strength of the samples. This was attributed to premature closure of voids, and hence higher porosity and low final density of such samples [27]. Also, attempts have been made to combine micron sized whiskers of chopped fibers with preceramic polymer, where whisker-fiber CMCs were developed [6].

1.1. Nanotechnology

The field of nano-composites involves the study of multiphase material where at least one of the constituent phases has one dimension less than 100 nm. This is the range where phenomena associated with atomic and molecular interaction strongly influence the macroscopic properties of materials. Since the building blocks of nano-composites are at nanoscale, they have an enormous surface area and there are a great deal of interfaces between the two intermix phases. The special properties of the nano-composite arise from the interaction of its phases at the interfaces and inter-phases. By contrast, in a conventional composite based on micrometer sized filler such as carbon fibers, the
interfaces between the filler and matrix constitute a much smaller surface-to-volume fraction of the bulk materials, and hence influence the properties of the host structure to a much smaller extent. The promise of nano-composites lies in their multifunctionality, the possibility of realizing unique combination of properties unachievable with traditional materials. The challenges in reaching this promise are tremendous. They include control over the distribution in size and dispersion of the nanosize constituents, tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties.

Recently researchers have investigated nano-composites containing polymer nanoparticles to improve their physical, mechanical, and chemical properties. Nanoparticles embedded in polymer matrix have attracted increasing interest because of the unique properties displayed by nanoparticles and their inclusion in polymers. Due to the nanometer size of these particles, their physicochemical characteristics differ significantly from those of micron size and bulk materials. When two or more phases are mixed together to make a composite, one can often obtain a combination of properties that are not available in either one constituent [28]. Also, concentrations of nanoparticles within the polymer matrix are of importance. Studies have shown that nanoparticles tend to agglomerate and create micro-particles when concentrated higher than their threshold, which could reduce the flexural strength of the nano reinforced CFCCs [29, 30]. Attempts have also been made to develop high performance nano-resins and nano-composites via the use of carbon nanotubes within the composite structure [31]. It has been successfully shown that a 3D multifunctional nano-composites can be manufactured using carbon nanotube coated fabric cloth, within each lamina, where samples
interlaminar mechanical properties and delamination resistance were substantially increased [32,33]. The carbon-nanotube forests allow the fastening of adjacent plies in the 3D composite creating a velcro-like effect.

1.2. Continuous Fiber Ceramic Composites by PIP

In the PIP process, the matrix polymer is first impregnated into the fiber architecture of choice and then cured by conventional methods. Both the initial shaping and fabrication of the composite are carried out with low-temperature polymer processing equipment. The composite is then pyrolyzed to temperatures greater than 1000 degrees C to convert the preceramic matrix polymer to a ceramic. Subsequent cycles of impregnation and pyrolysis steps are carried out to achieve the desired final density or open porosity.

1.3. Motivation

One of the important areas of concern is that even the best processed ceramic materials used in applications, pose many unsolved problems. Among them, relatively low toughness and strength, degradation of mechanical properties at high temperatures, and poor resistance to creep, fatigue, and thermal shock. Attempts to solve these problems may involve incorporating second phases such as particulates, platelets, whiskers, and fibers in the micron and nanometer size range at the matrix grain boundaries. However, results have been generally disappointing when micron-size fillers are used to achieve these goals [27-28]. Traditional polymer composites filled with micrometer size fillers often show improvements in their mechanical properties in the form of increases in modulus and glass transition temperature [29-30].
However, these gains are usually accompanied by losses in ductility, toughness and often strength. In addition, large amounts of filler are often required to achieve the desired properties, often diminishing the weight savings gained in using low-density polymers [29]. By scaling the particle size to the nanometer scale, it has been shown that novel material properties can be obtained. Recent research indicates that the dispersion of sub-micrometer and nanometer sized inorganic particles presents a novel approach towards improving the mechanical properties of polymers. Such materials, which include polymer nanocomposites, have the potential for significantly enhanced and unique properties as compared to polymers reinforced with conventional microscale fillers [31]. However, a critical parameter in controlling the mechanical properties of any nanocomposite depends on the dispersion state and concentration of the nanoparticles [32]. It has been shown that nanoparticles tend to agglomerate because of their high surface area and energy [33-35]. Dispersing metallic second-phase particles into ceramics improves their mechanical properties [36]. In addition, the nanoparticles can lend properties to the polymers that they cannot achieve alone or with traditional fillers. Materials that cannot be grown easily as single-crystals can be used at the nano-scale and dispersed in a polymer to take advantage of the single crystal properties. Optimized processing can lead to excellent structural control at the molecular level in most nano-composite materials. A wide variety of properties, including magnetic, electric, thermal, and optical properties, can also be tailored in nano-composites due to the size effect of nano-sized dispersions [28, 37-41]. Such materials can be produced by incorporating a very small amount of nano-sized inclusion into the ceramic matrix. Another approach would be the inclusion of nano materials on the surface of the fabric to reinforce the interlaminar space where matrix
originally employs. Carbon nanotubes have shown to provide excellent interlaminar flexural properties compared to composites without any nano reinforcements within the matrix [42]. Therefore, in this work, Continuous Fiber Ceramic Composites (CFCCs) were manufactured using KiON CERASET preceramic polymer [43] without nanoparticles, with nanoparticles only, with carbon nanotubes only, and with a combination of nanoparticles as well as carbon nanotubes. The nanoparticles used in this work, were yttrium oxide with an average size of 27 nm. The carbon nanotubes used, had an average length of 40 nm and were grown directly on the surface of Nicalon™ ceramic grade silicon carbide plain weave fabric [44].

The effects of nanoparticle and carbon nanotube reinforcements on processing and flexural mechanical performance of CFCCs using PIP were investigated and reported. Among the nano reinforcements used, the combination of yttrium oxide nanoparticles and carbon nanotube reinforcements performed the best in terms of nanocomposites property enhancement. Significant improvements in the in-plane mechanical properties of carbon nanotubes (CNTs) or nanoparticles reinforced composites compared to their unreinforced counterparts have been reported [32, 38].

The optimum amount of nanoparticles in the composites was 15wt% desperesed uniformly within the preceramic polymer. Here, we report an experimental investigation on the effects of combined yttrium oxide nanoparticle and carbon nanotube nanoforest reinforcements, on the processing and flexural properties of CFCCs.
1.4. Goals of this Research Effort

The primary objective of this research was to manufacture SiC/SiC, CFCCs employing preceramic polymer pyrolysis/reinfiltration (PIP) route. Other goals of this research were: i) To investigate the influence of nanoparticle as well as carbon nanotube reinforcements on flexural mechanical performance of CFCCs, and ii) To determine the improvements in mechanical properties of the combination of nanoparticle and carbon nanotube nanoforest reinforced CFCCs. Mechanical performance of CFCCs were evaluated using four-point bending test. SEM micrographs and processing results were used to determine the part quality and performance of the manufactured specimens.

1.5. Organization of Thesis

The first chapter contains a general introduction to CFCCs, nanotechnology, and the motivation for the current study. The manufacturing methodology, employed for the manufacturing of the CFCCs used in this study are discussed in Chapter 2. A detailed description of the manufacturing process involved, followed by a description of manufacturing route for different types of samples are presented in Chapter 3. Quality assessment, and processing results for different CFCC samples are discussed in Chapter 4. Chapter 5 presents the four-point flexure test results for different sets of nano-reinforced CFCC specimens, followed by comparison of mechanical property improvements for nano-reinforced CFCCs. Finally, conclusions are made in Chapter 6.
CHAPTER 2

MANUFACTURING METHODOLOGY & MATERIAL SYSTEM

2.1. Introduction

The Polymer Impregnation & Pyrolysis (PIP) process used to fabricate CFCCs is widely recognized as a versatile method to fabricate large, complex-shaped structures. In comparison with other ceramic composite fabrication processes, the PIP process offers significantly greater flexibility. By utilizing low temperature forming and molding steps typically used in organic matrix composites, the PIP approach allows one to use existing equipment and processing technology to form the parts.

2.2. Preceramic Polymer Technology

When the field of producing ceramics by preceramic polymer pyrolysis was emerging in the late 60’s and early 70’s, very few precursors were known. At that time, various carbon products were used. A review of the history of producing non-oxide ceramics from polymer pyrolysis is presented by Rice [15]. An investigative study was carried out to identify other precursors and structure-yield trends, and determine the potentiality of producing ceramics via the preceramic polymer pyrolysis route.

The pyrolysis of organometallic polymers, or other precursors was found to be a novel method to manufacture ceramics. This extremely useful technique is widely applicable to include silicon carbide, silicon nitride, and boron nitride ceramics. Instead of using
carbon polymers, silicon-based polymers are used to produce ceramics with high yield. The polymer-derived ceramics that can be produced by preceramic polymer pyrolysis include fibers, matrices, and coatings.

In preceramic polymer technology, a polymer is used as a starting material. Since a polymer is used as a precursor, conventional polymer manufacturing techniques can be utilized to fabricate ceramics and ceramic matrix composites. These methods include resin transfer molding, filament winding, pultrusion, wet lay-up using autoclave, etc. The part is shaped in the polymer condition using conventional manufacturing techniques, then cured and cross-linked to stabilize the shape of the part and finally is pyrolyzed to partially convert the polymer into a ceramic. During the pyrolysis, a portion of the polymer burns out and produces some combustion products that must be extracted from the furnace. This leaves the part with some porosity that must be overcome with subsequent reinfiltration and pyrolysis iterations through the cracks developed by residual stresses until the density convergence through a weight gain criterion is achieved.

Pyrolysis is the necessary step of heating the part in order to convert the polymer matrix into a stable ceramic phase. This is carried out in a high temperature furnace under a non-reactive gaseous, i.e., inert environment. Inert gases such as argon and nitrogen are used in preceramic polymer pyrolysis. Repeated infiltration steps are carried out to increase the density of the composite. With preceramic polymer fabrication, the number of infiltration steps used to fill the voids and pores caused by pyrolysis controls the density and porosity of the composite. The number of infiltration-pyrolysis steps range from 4 –10 depending on the fiber material and char yield of the polymer. Densities of preceramic polymers typically
range from 1.1 to 1.2 g/cm$^3$, with weight-based char yields ranging from 60% to over 90%.

The use of preceramic polymers overcomes many problems in processing conventional binders, including high part rejection rates and low part reliability. This technology has the advantage of fabricating and forming fiber-reinforced ceramic matrix composites that were difficult to make via conventional binder techniques, and improvements in the CMC processing technique such as lower processing temperature.

Preceramic polymer technology in conjunction with wet lay-up opens the possibility of manufacturing complex-shaped CFCC’s, which are tougher and stronger than their short fiber CMC counterparts.

### 2.3. Wet Lay-up Process

In the early days, the wet lay-up process was the dominant fabrication method for the manufacturing of composite parts. It is still widely used in the marine industry as well as for making prototype parts. This process is labor intensive, where liquid resin is applied to the mold and reinforcement and the process is continued until a desired thickness is obtained. It is a very flexible process that allows the user to optimize the part by placing different types of fabric and mat materials. Since the reinforcement is placed manually, it is called the hand lay-up process. This process requires little capital investment and expertise and is therefore easy to use [42].

There are four basic steps involved in a wet lay-up process of composites: wetting/impregnation, lay-up, consolidation, and solidification. All composites manufacturing processes involve more or less the same four steps, although they are
accomplished in different ways. During the impregnation stage, the fibers and resins are mixed together to form a lamina. In this process, each fabric layer is wetted with resin using a squeezing roller for proper impregnation. The purpose of this step is to make sure that the resin flows entirely around all fibers. Viscosity, surface tension, and capillary action are the main parameters affecting the impregnation process. During the Lay-up stage, the desired composite thickness is built up by stacking various layers of wetted fibers on top of each other until the desired thickness is obtained. Performance of the composite structure relies heavily on fiber orientation and lay-up sequence.

Consolidation involves in creating intimate contact between each layer of prepreg or lamina. This step ensures that all entrapped air is removed from the in-between layers by resin flow during the processing. Consolidation is an important step to obtain good part quality. Poorly consolidated parts will have voids and dry spots. Proper consolidation is obtained when the applied pressure is equally shared by both the resin and fiber structure. The final step is solidification, which may take less than a minute for thermoplastics or may take up to 120 minutes or more for thermosets. Vacuum and/or pressure is maintained during the period. The lower the solidification time, the higher the production rate achievable by the process. In thermoset composites, the rate of solidification depends on the resin formulation and cure kinetics. Heat is supplied during processing to expedite the cure rate of the resin and initiate linking in some cases.

On a commercial scale, this process is widely used for making boats, windmill blades, storage tanks, and swimming pools. Due to its process simplicity and little capital investment, this process is widely used for making prototype parts. Test coupons for
performing various tests for the evaluation of reinforcements as well as resins are also made using this process [42].

2.4. Materials System

2.4.1. Preceramic Polymer

The inorganic polymer used in this study is KiON CERASET® [43] preceramic polymer. KiON CERASET® materials are novel patented liquid compositions which enable the fabrication of silicon carbide, silicon nitride, and silicon carboxide monolithic ceramics or composites. The final composition of the composite depends on the pyrolysis cycle and inert gas used. During the pyrolysis, nitrogen or argon, ammonia, and air environment produces a silicon carbide, silicon nitride, and silicon carboxide ceramic matrix, respectively. In this work, argon gas was used to produce silicon carbide matrix. The low molecular weight, thermosetting Polyureasilazane combines the processing flexibility of liquids with the high pyrolytic yields previously demonstrated by higher molecular weight, thermoplastic precursors. This polymer contains repeat units in which silicon and argon atoms are bonded in an alternating sequence. The polymer can be prepared in a continuum of viscosity from 30 centipoises through 30,000 centipoises, which helps in tailoring the polymer for a specific processing technique by heating the resin below cure temperature. This low viscosity polymer is thermoset (cured) to a solid by heating to 180-200 °C. Cure can be affected at lower temperatures through the addition of a small amount of a free radical initiator such as organic peroxide. Around 0.1 to 5 wt% of peroxide is sufficient to initiate cure. Dicumyl peroxide obtained from Aldrich Chemical® [44] is used as the free radical initiator in this
work. Typical ceramic yields, an indication of mass conversion to ceramic material, as measured by thermal gravimetric analysis (TGA), is about 75% for KiON CERASET® in nitrogen and argon, and about 95% in air [43]. Table 2.1 shows the physical properties of KiON CERASET®.

Table 2.1: Properties of KiON CERASET® [43]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>-78 ºC</td>
</tr>
<tr>
<td>Boiling point</td>
<td>150 ºC</td>
</tr>
<tr>
<td>Viscosity, 25°C / 50°C / 75°C / 100°C</td>
<td>50 cp / 30 cp / 20 cp / 15 cp</td>
</tr>
<tr>
<td>Density of liquid</td>
<td>0.96 g/cm³</td>
</tr>
<tr>
<td>Density of ceramic from pyrolysis of cured polymer</td>
<td>2.4 g/cm³</td>
</tr>
<tr>
<td>Incompatible Reagents</td>
<td>acids, bases, water, alcohols</td>
</tr>
</tbody>
</table>

2.4.2. Fiber Selection

Nicalon™ ceramic fiber was chosen as the fiber system reinforcement. Nicalon™ is a silicon carbide (SiC) type fiber and has a desirable combination of modulus, strength, density, and electrical properties with retention of these properties at elevated temperatures up to 1400 ºC. Nicalon™ is black in color and has a composition of 58% silicon (Si), 31% carbon (C), and 11% oxygen (O) [44]. The architecture of the fiber is a plain weave cloth with 16 tread count/inch in both warp and weft directions. A list of physical properties of the fibers is listed in Table 2.2.
2.4.3. Nanoparticle Reinforcements

The nano-sized inclusions used in this work to reinforce the matrix are yttrium oxide (Y2O3) nanoparticles in nano-powder form. These particles are insoluble in water and stable in air. Table 2.3 gives the specifications of the yttrium oxide nano particles.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Y2O3 [45]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>5.01</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>29</td>
</tr>
<tr>
<td>Melting Point (0C)</td>
<td>2425</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
</tr>
<tr>
<td>Surface Area (sq.m/gm)</td>
<td>42</td>
</tr>
</tbody>
</table>

Glycerol monooleate obtained from BASF Corporation [46] is used as surfactant agent. Glycerol monooleate was mixed with preceramic polymer to provide good dispersion of nanoparticles in KiON CERASET®. In this work, “Pristine” refers to a base composite with no nano particles reinforcements and “Pristine + NP” refers to a base composite where the matrix is reinforced with 15wt% yttrium oxide nanoparticles. Subsequently,
“Pristine + NF” refers to a base composite where the fibers are reinforced utilizing the carbon nanotube nanoforest technology [32] and “Pristine+NP+NF” refers to a base composite reinforced with both yttrium oxide nanoparticles as well as carbon nanotube nanoforest.

The NP reinforced specimen are manufactured with preceramic polymer infiltration pyrolysis (PIP) route, where the matrix for the initial forming as well as the first 2 reinfiltiration cycles has nanoparticles inclusions and the rest of the infiltration matrix for the remaining densification cycles does not.

2.4.4. Carbon Nanotube Nanoforest Reinforcements

The nano-sized insertions used in this work to reinforce the fibers are vertically aligned carbon nanotubes. These nanotubes are grown perpendicular to the surface of the ceramic grade Nicalon™ fabric and parallel to each other, in a dense and uniform manner called nanoforest (NF). This technology, demonstrates the extraordinary strengths that carbon nanotubes exhibit in their longitudinal direction and can be used to reinforce the space in between the fibers where pure pristine pre-ceramic polymer matrix originally exists. This gives the ceramic composite, a through the thickness strength by creating a matrix interface of interlocking carbon nanotubes extending outward from the top and bottom surfaces defined by each lamina, creating a 3-D composite laminate.

The length of the carbon nano-tubes used in this work, are in the range of 30 to 50 um with the diameter of each carbon nanotube (multi-walled) in the order of 70 nm. The nanotubes are grown directly on the ceramic grade Nicalon™ fabric which are stacked up utilizing the wet lay-up manufacturing technique followed by curing via the
compression molding process. Specimens with only carbon nanotube nanoforest “Prisitne+NF” and a combination of carbon nanotube nanoforest and yttrium oxide nanoparticles “Prisitne+NP+NF” were manufactured to be compared and analyzed along with other specimens mentioned in Section 2.4.3.
CHAPTER 3

MANUFACTURING PROCESS

3.1. Introduction

The manufacture of Continuous Fiber Ceramic Composites by Hand Lay-up using Polymer Impregnation Pyrolysis consists of two steps as shown in the flow chart given later in this chapter. The first step involves impregnating the fiber preform with preceramic polymer and stacking them on top of each other to achieve a desired thickness, followed by compression molding (see in Fig.3.1) and curing in the hot press (see Fig. 3.2).

The second step consists of pyrolyzing the cured sample, thereby converting the preceramic polymer into ceramic (in a high-temperature furnace shown later in this chapter), followed by subsequent reinfiltration/pyrolysis cycles to achieve weight convergence.

3.2. Manufacturing of CFCC specimens for Mechanical Testing

3.2.1. Wet Lay-up of Fiber Cloths

Plain weave Silicon Carbide and Carbon fiber cloths are used as the fiber architecture for the manufacturing of the mechanical test specimens. KiON CERASET® preceramic polymer is the matrix used in the current study. The thickness of the fiber preform was measured using a micrometer, which was approximately 0.0125” for the SiC cloth. The preform was cut into dimensions of 6” x 4” layers from the roll.
For the manufacturing of the mechanical test samples, 3 layers of SiC were used for each plate. In this process, initially each layer of fiber preform is properly impregnated with the polymer. Special care was taken to wet the fibers with sufficient amount of polymer for a good bonding between the laminae. After wetting the fiber preform, the wet laminae were stacked on top of each other and, subsequently, pressed using a roller until a desired thickness was obtained. Also, a foam brush was used to remove all the excess resin before and after lay-up.

3.2.2. Compression Molding and Curing

This section of the thesis explains the compression molding and curing process. To manufacture the composite plates, two appropriate aluminum plates were selected. A one millimeter deep rectangular trench with dimensions of 6” x 4” was milled out of one plate to serve as a mold and the other plate was untouched and used as the cover plate. This mold is shown in Figure 3.1. Next, the mold was sand gritted with 220 grit paper (coarse) and then with 400 grit paper (fine) in a circular motion and degreased with acetone. A thin layer of high temperature polishing wax is applied on the plate and left for a few minutes, followed by removal of it using a lint free cloth for better surface finish on the specimens. Dry mold release agent was then sprayed on the plate for easy removal of the part after the manufacturing.
After initial preparation of the base plate and the cover plate, the wet lay-up stacked laminae is placed in the mold cavity and then covered with the cover plate. The mold is then put in the compression molding machine for curing and consolidation as shown in Figure 3.2 below.
Samples are cured at the maximum temperature of 200 °C under uniform pressure of 120 psi. Figure 3.3 shows the cure profile used in this work.

![Cure Profile](image)

Figure 3.3: Compression molding machine cure cycle (Note: no vacuum was applied).

Before curing (B-staging) starts, pressure was applied by the compression molding top and bottom plates first and temperature was raised to a dwelling level. The temperature rise was from room temperature to 200 degrees C in 1 hour, dwelled for 1 hour and cooled to room temperature in 1 hour. Hence, the total cycle time was 3 hours. The maximum heating rate of the Compression Molding Machine was 5 degrees C/min. After the cooling, the cured laminate is removed from the mold as shown in Figure 3.4. The consolidated green ceramic plates were then ready to be cut and weighed before densification.
The edges of the manufactured plate after B-Staging were trimmed off and the samples were cut according to ASTM C 1341 [47] in required dimensions for mechanical testing (see Figure 3.5).

At this stage, specimens are ready to be densified via Polymer Infiltration and Pyrolysis (PIP) route.

3.2.3. Pyrolysis / Reinfiltration / Pyrolysis

After B-staging, cutting, and initial weighing, the cut laminates were then pyrolyzed in a high temperature tube furnace, as seen in Figure 3.6, in an inert environment to convert the polymer into ceramic.
The thermal cycle for the pyrolysis is as shown in Fig.3.7. The samples were heated from room temperature to 100 °C at a heating rate of 2 °C/min, dwelled at 100 °C for 2 hours, ramped from 100 °C to 700 °C at a rate of 10 °C/min, dwelled at 700 °C for 1 hour, ramped from 700 °C to 1000 °C at a rate of 5 °C/min, dwelled at 1000 °C for 1 hour. The furnace was then allowed to cool down at a rate of 3 °C/min to 250 °C under inert argon gas environment. The samples were finally allowed to cool down to room temperature by natural convection. The total cycle time for each pyrolysis step was approximately 15 hours. The test samples were then removed from the furnace, weighed, and measured again.
Pyrolyzed parts were immersed in preceramic polymer for reinfiltration. Reinfiltration is necessary to increase the part density and fill the voids and microcracks inside the samples created by matrix shrinkage and conversion of polymer to ceramic during the pyrolysis step. The samples were allowed to stay in the polymer until all the bubbling subsided in the reinfiltration stage, which took 6-8 hours. Once the bubbling subsided, the samples were removed from the preceramic polymer, wiped free of excess resin, weighed, and placed on top of a polished aluminum plate. The plate was then placed inside a mechanical convection oven and cured according to the cure cycle previously outlined, without pressure. After the curing, the samples go through a pyrolysis stage in an inert environment according to the pyrolysis thermal cycle previously outlined. After this stage, the samples received their first densification, i.e., State 1. This densification cycle was repeated eight more times until the samples were fully densified. All the samples manufactured converged in weight gain according to the weight convergence criterion used. The criterion for weight gain convergence was that the last sequential weight gain of the samples should be less than 1%. The total manufacturing time for a CFCC sample was around 9 days. Figure 3.8 shows the general CFCC manufacturing methodology employed to manufacture the required test samples.
3.2.4. Vacuum Infiltration vs Passive Infiltration

In this work, a forced type of polymer impregnation was employed versus the traditional passive dipping method. As shown in Figure 3.9, a Pelican® case [48] was modified to be used as a vacuum container. Articles were placed in a pool of polymer inside the vacuum container, where after proper sealing; a 90% vacuum has been achieved. The vacuum pressure inside, forces the preceramic polymer deep into the pores of the specimens to ensure proper densification and to prevent premature closure on the surface of the specimens which would result in a porous CFCC.
3.3. Manufacturing Procedure for CFCCs

The general process of manufacturing continuous fiber ceramic composites can be explained by the following steps: wet lay-up, curing, and polymer pyrolysis/reinfiltration cycles. The above process was explained in detail in Section 3.2. To evaluate the effects of nano reinforcements on processing and flexural mechanical properties, 4 types of CFCCs were manufactured. All laminates consisted of 3 layers of plain weave SiC cloths of 0.318 mm in thickness, which were cut from the fabric lot to achieve the desired thickness of 1 mm. These include, “Pristine”, “Pristine + NP”, “Pristine + NF” and “Pristine + NP + NF”. Detailed descriptions of each type are given in Section 2.4.3. Nicalon™ fibers and KiON CERASET® preceramic polymer were used in all of the 4 types.
3.3.1. Manufacture of Pristine SiC CFCCs

In this work, “Pristine” SiC CFCCs consists of SiC fabric and preceramic polymer only without any type of nano-reinforcements and is used to establish a baseline for comparison with nano-reinforced SiC CFCCs. Three layers of SiC fabric is wetted with preceramic polymer and is stacked up using the wet lay-up technique, followed by curing using the compression molding machine. Next, the edges of the laminated composite plates are trimmed and samples of required dimensions (ASTM C 1341-06) are cut using a diamond blade cutter. The cut samples are then pyrolyzed in a high temperature tube furnace in an inert argon gas environment to convert the preceramic polymer into ceramic. To convert the porous ceramic after the first pyrolysis step, subsequent reinfiltration/pyrolysis are followed as outlined previously to achieve the required dense CFCC test specimens. The manufacturing process remains the same as explained in Section 3.2.3 and is shown in Figure 3.8.

3.3.2. Manufacture of SiC CFCCs Reinforced with Y2O3 Nanoparticles

Two different systems of CFCCs with Nanoparticle reinforcement were manufactured. As explained in Section 2.4.3, “Pristine + NP” refers to sample reinforced with nanoparticles only and “Pristine + NP + NF” refers to sample reinforced with both nanoparticles and carbon nanotube nanoforest. For both cases, 15wt% of yttrium oxide nanoparticles were mixed with Glycerol monooleate used as a surfactant agent and then mixed with preceramic polymer. To provide good dispersion of nanoparticles in KiON CERASET®, the mixture is then sonicated for duration of 30 minutes to encourage uniform and proper dispersion. The above matrix is used to wet lay-up the laminate. The
laminate is at the green stage after curing. The manufacturing process remains the same as explained in Section 3.2.3, except for the use of nanoparticle reinforced preceramic polymer as shown in Figure 3.10. The average size of yttrium oxide nanoparticles were 27 nm. It is important to note that in the reinfiltration process, after the second cycle, neat preceramic polymer without any nanoparticle reinforcement is used.

![Nanoparticle filled CFCC manufacturing methodology.](image)

3.3.3. **Manufacture of SiC CFCCs Reinforced with Carbon Nanotube Nanoforest**

In this study, the manufacturing process remains the same as mentioned in Section 3.3.1, except for the use of carbon nanotube nanoforest grown on top of the SiC fabric as a fiber
reinforcement. In this case, carbon nanotubes were grown using Chemical Vapor Deposition (CVD) for a period of about 30 minutes. This creates a uniform and dense field of carbon nanotubes with an average length of 40 microns on the top and bottom surfaces of the fabric. Neat preceramic polymer is used for the reinfiltration of the “Prisitne + NF” samples. All other manufacturing steps remain the same as explained earlier. Manufacturing process for carbon nanotube reinforced CFCCs is shown in Figure 3.11.

Figure 3.11: Carbon nanotube reinforced CFCC manufacturing methodology.
3.3.4. Manufacture of SiC CFCCs Reinforced with Y2O3 Nanoparticles and Carbon Nanotube Nanoforest

This type of CFCC is labeled as “Prisitne + NP + NF” where a combination of nanoparticle reinforcement to reinforce the matrix as explained in Section 3.3.2 and carbon nanotube nanoforest reinforcement to reinforce the fibers as explained in Section 3.3.3 were used. All other manufacturing steps remain the same. Figure 3.12 shows the process flow diagram for CFCCs reinforced with both nanoparticles and carbon nanotubes.

![Process Flow Diagram](image)

Figure 3.12: Nanoparticle and carbon nanotube reinforced CFCCs manufacturing methodology.
CHAPTER 4

PROCESSING RESULTS, CHARACTERIZATION, AND DISCUSSION

4.1. Quality Assessment and Characterization of the CFCC test samples

In this study, analysis using scanning electron microscopy (SEM) was performed to characterize and examine the quality and distribution of both of the nano-reinforcements, first the carbon nanotube nanoforest grown on the surface of the Nicalon® SiC fabric followed by the dispersion pattern of Yttrium oxide nanoparticles. Figure 4.1 compares plain fabric image with carbon nanotube nanoforest grown on the fabric obtained using SEM.

Figure 4.1: SEM images of Nicalon SiC fabric: a) top view of plain fabric, b) top view of fabric with grown carbon nanotube nanoforest reinforcement, and c) top view of fabric with grown carbon nanotube nanoforest reinforcement with higher magnification.
After characterization of the grown carbon nanotubes and verification of uniform growth, samples were manufactured. Dispersion of Y2O3 nanoparticles in preceramic polymer is also an important factor in the performance of nanoparticle-reinforced nanocomposites; therefore, its dispersion had to be analyzed. Improper dispersion leads to agglomeration of nanoparticles and the agglomerated inclusions act as defects with high stress concentrations, instead of acting as uniform reinforcements. To study the dispersion of nanoparticles in CERASET®, the polymer was mixed with the 15 weight percentage of nanoparticles and 5-wt% of surfactant glycerol Monooleate using the sonicator machine. The nanoparticle filled preceramic polymer was then cured according to the procedure outlined to thermoset the liquid polymer using vinyl cross-linking mechanism. As shown in Figure 4.2, the SEM studies revealed uniform dispersion of weight percentage of 15% without any agglomeration.

Figure 4.2: Uniform dispersion of 15wt% Y2O3 nanoparticles.

After dispersion verification, manufacturing and PIP processing continued according to procedures mentioned previously.
4.2. Processing Results for Manufactured Pristine and Nano-Reinforced CFCCs

This section details and analyzes the processing results for continuous fiber ceramic composites manufactured using neat preceramic polymer only (Pristine), followed by the use of two different types of nano reinforcements (i.e., Pristine+NP, Pristine+NF), and the combination of the two types of nano-reinforcements (i.e., Pristine+NP+NF). In this work for each sample, a gain in weight of less than 1% from previous pyrolysis/reinfiltration cycle was considered as the convergence criterion. The difference in weight for the samples after the first and the last (in this case, ninth) pyrolysis/reinfiltration cycle is reported as cumulative percentage weight gain in Table 4.1.

Table 4.1: Processing results for manufactured CFCCs.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Weight Gain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>30.96</td>
</tr>
<tr>
<td>Pristine+NP</td>
<td>34.76</td>
</tr>
<tr>
<td>Pristine+NF</td>
<td>40.31</td>
</tr>
<tr>
<td>Pristine+NP+NF</td>
<td>53.48</td>
</tr>
</tbody>
</table>

In addition, Figure 4.3 plots the cumulative weight gain percentages of the four types of CFCCs against pyrolysis/reinfiltration cycles. It can be seen that “Pristine+NP” had the highest overall percentage of weight gain due to inclusion of nanoparticles in the first infiltrations. “Pristine+NP” followed the same pattern as “Pristine” but with higher cumulative weight gain due to the presence of NPs, which shifted the “Pristine” curve up. “Pristine+NF” also followed a fairly similar pattern as “Pristine”, having a higher weight accumulation compared with “Pristine” and lower compared with “Pristine+NP”.

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“Pristine+NP+NF” had the same weight gain behavior as the rest of the CFCCs with slightly higher initial weight gains also due to use of nanoparticles in the initial reinfiltration cycle. However, weight accumulation slowed down possibly due to the interaction of carbon nanotube and nanoparticles. Initially all CFCCs lost the same amount of the weight of about 20% during the first pyrolysis cycle, therefore demonstrating the same char yield as shown in Figure 4.3 at the first pyrolysis cycle.

Figure 4.3: Comparison of cumulative weight gain (%) for different types of CFCCs after each pyrolysis cycle.

Furthermore, all CFCC samples manufactured took the same number of pyrolysis/reinfiltration cycles to achieve the weight gain convergence. Therefore, adding nanoparticles to the matrix and carbon nanotubes to the fibers did not affect the processing of the CFCCs, while it is known that, adding micron-size particle reduces the number of reinfiltration/pyrolysis due to a possible premature closure which results in higher porosity, lower density, and lower strength [27, 32]. This suggests that the nanoparticles reinforcements, when done at the first iteration with high percentage of nanoparticles, do not cause premature closures since the number of
reinfiltartion/pyrolysis cycles required to achieve weight gain convergence with and without nanoparticle and carbon nanotube reinforcements remained the same.
CHAPTER 5

MECHANICAL PERFORMANCES

5.1. Introduction

The main objective of this part of the study is to experimentally evaluate the mechanical performance and failure mechanism of different CFCC specimens in flexure. A four-point bend fixture was used to measure the flexural load-deflection response of CFCC specimens loaded in four point bending. The test specimens, as seen in Figure 5.1, were selected so that they had a span to depth ratio \((L/d)\) that produces tensile and compressive stresses at the outer surfaces of the sample under the bending loading. In this study, the \(L/d\) value is 40.0. All specimens were nominally 50 mm long, 3 mm wide, and on an average 1 mm thick. Five samples were used for each type of CFCC flexure test. The tests were conducted using an Instron testing machine.

![Figure 5.1: Typical manufactured CFCC test specimens.](image)

Test method for flexural properties of continuous fiber reinforced advanced ceramic composites, ASTM C 1341 [47], is used to determine the flexural properties of the CFCC specimens in the form of rectangular bars. Figure 5.2 shows a schematic of the four-point...
flexure test. The test specimen rests on two supports, the distance between which is called support span. The specimen is loaded at two points by means of two loading rollers, which are situated one third of the overall span away from the outer two support bearings (see Figure 5.2). The distance between the loading rollers, i.e., the load span is one third of the support span. The support span length was 40 mm and load span length was 13.3 mm.

![Figure 5.2: Schematic of four-point flexure test, ASTM C1341 [47].](image)

Flexure test provides information on the strength, stiffness, and deflection/strain-to-failure of materials and structures under complex flexural stress conditions. In CFCCs, complex stress-strain behavior may develop as a result of cumulative damage processes; for example, matrix cracking, matrix/fiber debonding, fiber pull-out, fiber fracture, and delamination. This may be influenced by testing mode, testing rate, processing effects, or environmental influences. Some of these effects may be consequences of stress corrosion or sub-critical (slow) crack growth, which can be minimized by testing at sufficiently rapid rates. In this study, the test rate was 1.18 mm/sec [47]. The maximum stress in the outer surface at the point of maximum stress, i.e., flexural strength \( S \) can be calculated using the maximum load and deflection obtained from the four-point flexure test, and is given in Equation (1) [47]:

\[
S = \frac{PL}{bd^2}
\]  

(1)
where, $P$ is the maximum load in the flexure test in Newton (N), $b$ is the specimen width in mm, $d$ is the specimen thickness at the point of break in mm, and $L$ is the length of the specimen in mm. Equation (2) gives the flexural modulus of elasticity, $E$, for samples tested in four point flexure [47]:

$$E = \frac{0.21mL^3}{bd^3}$$

Equation (2) gives the flexural modulus of elasticity, $E$, for samples tested in four point flexure [47]:

where, $m$ is the slope of tangent to the initial straight-line portion of the load-deflection curve (N/mm). Similarly, the maximum strain-to-failure was calculated using Equation (3).

$$\varepsilon = 4.7\left(\frac{Dd}{L^3}\right)$$

where, $D$ is the deflection in mm. Toughness refers to the amount of energy per unit volume that a material can absorb up to failure. As seen in Equation (4), toughness was calculated using Equations (1) and (3).

$$\frac{\text{energy}}{\text{volume}} = \int_0^{\sigma_f} \sigma \cdot \delta \varepsilon = \frac{2.35PD}{bdL}$$

Four-point bending test was chosen to quantify the performance of CFCCs as shown in Figure 5.3. The four-point geometry is known to produce more reliable statistical data when compared with three-point bending test, particularly for brittle materials [26]. For obtaining a valid flexural strength by four-point bending test, a high support span/thickness ($L/d$) ratio of about 40 was used to prevent shear failure and invalidation of the tests.
The primary reason that four-point bending test [47] is preferred over three-point bending test [47] for brittle materials, is that for three-point bending test, the moment diagram is maximum under the loading point (see Figure 5.4) and this causes stress concentrations under maximum stress that could lead to a premature failure.

Whereas, in case of four-point bending, the stress concentrations of three-point bending at the potential failure location (i.e., mid-span) does not exist and the mid-span (i.e., where the stress is maximum) is not directly under the loading. In addition, in the four-point bending test, the moment diagram is maximum and constant in between the load span (see Figure 5.5), leading to more distributed stress in between the supports with lower stress at the mid-span and higher stress in between the supports (as compared to the three-point bending test) and hence more of the specimen’s cracks in between the supports.
supports are subjected to higher stresses, on the average, and hence a more reliable failure may occur in this case for brittle material.

![Figure 5.5: Moment diagram for 4-point bending test.](image)

All the tested samples fractured inside the uniformly stressed region of flexure specimen (i.e., between the inner loading points of the fixture), eliminating uncertainties about failures due to stress concentrations outside the uniform loading region as well as the shear failure of the specimen (see Figure 5.6).

![Figure 5.6: A typical sample failed at its mid-span.](image)

### 5.2. Four-point Flexure Tests, Results and Discussion for the Pristine CFCCs

This section reports and analyzes the results of the four-point bending tests for “Pristine” CFCCs. These samples did not have any type of nano-reinforcements and were used to establish a baseline. Total of five specimens were tested using the Instron testing machine. The load-deflection curves for “Pristine” test specimens are shown in Figure 5.7.
“Pristine” test specimens showed very uniform pattern to failure, demonstrating the uniform quality of the CFCCs as well as the accuracy of the baseline data. All specimens failed within the uniform loading region (i.e., between the inner loading points of the fixture) as predicted. Table 5.1 reports the average of maximum load, maximum deflection \(D\) at beam center at maximum load, and the thickness \(d\) at the point of break from the four-point bending test for Nicalon™ Fiber and KION CERASET® precresmic polymer mechanical test specimens. The standard deviation of load is given in parentheses.

Table 5.1: Four-point bending test results for “Pristine” Specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>(d) (mm)</th>
<th>Load (N)</th>
<th>(D) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>1.06</td>
<td>3.06 (0.33)</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Using Equations (1) thru (4) the flexural strength, modulus, strain to failure and toughness for all samples were calculated, respectively, and are reported in Table 5.2.
with their standard deviations in parentheses. Same trend as the load at failure is also observed for the flexural strength of the specimens.

Table 5.2: Mechanical properties from 4-point bending test results for “Pristine”.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Flexural Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Strain-to-failure (mm/mm)</th>
<th>Toughness (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>32.83 (3.06)</td>
<td>45.5 (5.66)</td>
<td>0.000643</td>
<td>12.4 (2.70)</td>
</tr>
</tbody>
</table>

5.3. Four-Point Flexure Tests, Results, and Discussion for Y2O3 Nanoparticle Reinforced CFCCs

This section reports and analyzes the results of the four-point bending tests for Yttrium oxide nanoparticle reinforced CFCC labeled as “Prisitne+NP”. Five different specimens were tested and averaged in this study as discussed before. Four point bending test was chosen to quantify the mechanical performance of nanoparticles filled CFCCs as shown in Figure 5.5. All the test parameters such as support span/thickness ($L/d$) ratio, loading rate and dimensions of the specimen remained the same as described in previous sections. Figure 5.8 shows the load-deflection curves obtained in the four-point bending test. The strain was later calculated at the mid-span of the test specimen and using strain gages as suggested in the ASTM standard [47]. The failure load is at the peak in Figure 5.8.
Figure 5.8: Load-deflection curves obtained for “Pristine+NP” from the four-point bending test.

Once again, test samples all followed an identical pattern, validating the quality of CFCCs as well as the accuracy of the test. All the tested samples fractured inside the uniform loading region of flexure specimen, eliminating uncertainties about failures due to stress concentrations outside the uniform loading region as well as the shear failure of the specimen. Table 5.3 reports the average of maximum load (N), maximum deflection (D) at the beam center at maximum load, and the thickness (d) at the point of break from the four-point bending test for “Pristine+NP” CFCCs. The standard deviation of the maximum load is given in parentheses.

Table 5.3: Four-point bending test results for “Pristine+NP” Specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>d (mm)</th>
<th>Load (N)</th>
<th>D (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine+NP</td>
<td>1.50</td>
<td>3.14 (0.25)</td>
<td>0.20</td>
</tr>
</tbody>
</table>

From Table 5.3, it can be seen that using nanoparticle-reinforced preceramic polymer (Pristine+NP) resulted in an increase in failure load for all test specimens compared to their counterparts (Pristine), which were manufactured following a neat preceramic
polymer reinfiltiration/pyrolysis cycle. On the other hand, due to solid state influence of the nanoparticles, deflection of the specimens were slightly lowered for “Pristine+NP” CFCCs.

Using Equations (1) thru (4), the flexural strength, modulus, strain to failure, and toughness, respectively, for all five samples tested were calculated, averaged, and reported in Table 5.4 with their standard deviations in the parentheses.

Table 5.4: Mechanical properties from 4-point bending test results for “Pristine+NP”.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Flexural Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Strain-to-failure (mm/mm)</th>
<th>Toughness (MJ/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine+NP</td>
<td>34.68 (4.06)</td>
<td>50.7 (3.80)</td>
<td>0.000573</td>
<td>11.3 (1.69)</td>
</tr>
</tbody>
</table>

Analyzing the data in Table 5.4, a significant increase in modulus and a general tendency of increase in flexural strength, when CFCCs are filled with nanoparticles, are observed. However, a slight decrease in toughness was observed due to a lower strain to failure compared to the pristine counterpart, which resulted from a decrease in deflection as mentioned earlier.

5.4. Four-Point Flexure Tests, Results, and Discussion for Carbon Nanotube Nanoforest Reinforced CFCCs

In this section, results of the four-point bending tests for carbon nanotube reinforced CFCC labeled as “Pristine+NF” are reported and analyzed. Five specimens were tested in the similar manner as the previous two types. Once again, the test parameters such as support span/thickness (L/d) ratio, loading rate and dimensions of the specimen remained the same as described in previous sections. Figure 5.9 demonstrates the load-deflection
curves obtained in the four-point bending test for five test specimens reinforced with carbon nanotubes reinfiltreted with neat preceramic polymer only.

Figure 5.9: Load-deflection curves obtained for “Pristine+NF” from the four-point bending test.

Strain gauge started at a negative value but the value of the load is correct, for the curve shown to the left of “0” Flexure extension. Table 5.5 gives the average of maximum load (N), maximum deflection (D) at the beam center at maximum load, and the thickness (d) at the point of break gathered from four-point bending test results for “Pristine+NF” CFCCs. The averaged values and standard deviations are given in parentheses in Table 5.5.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>d (mm)</th>
<th>Load (N)</th>
<th>D (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine+NF</td>
<td>1.14</td>
<td>4.94 (0.53)</td>
<td>0.26</td>
</tr>
</tbody>
</table>

From the results obtained, it is interesting to observe that by employing carbon nanotube reinforcement only, remarkable improvement in load bearing capability as well as
deflection-to-failure of the CFCCs can be achieved. Equations (1) thru (4) were used to calculate the mechanical properties of the carbon nanotube reinforced CFCCs in a similar fashion as the previous two cases described above. Averaged properties are reported in Table 5.6 below with standard deviations in the parentheses.

Table 5.6: Mechanical properties from 4-point bending test results for “Pristine+NF” specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Flexural Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Strain-to-failure (mm/mm)</th>
<th>Toughness (MJ/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine+NF</td>
<td>41.99 (2.54)</td>
<td>42.78 (7.17)</td>
<td>0.000955</td>
<td>19.1 (5.35)</td>
</tr>
</tbody>
</table>

The substantial increase in load bearing capability resulted in a substantial increase in flexural strength, strain to failure, and subsequently an increase in toughness.

5.5. Four-Point Flexure Tests, Results, and Discussion for Y2O3 Nanoparticles and Carbon Nanotube Nanoforest Reinforced CFCCs

In this section, the combination of yttrium oxide nanoparticles and carbon nanotube reinforcements labeled as “Pristine+NP+NF” are analyzed and discussed. Five specimens underwent four-point bending testing to quantify their mechanical performance, similar to the previous three cases. Once again, test parameters remained unchanged. Figure 5.10 demonstrates the load-deflection curves obtained in the four-point bending test for five test specimens reinforced with yttrium oxide nanoparticles and carbon nanotube nanoforest.
All specimens failed within the uniform loading region, in between loading supports. Table 5.7 reports the average of maximum load (N), maximum deflection (D) at the beam center at maximum load, and the thickness (d) at the point of break from the four-point bending test for “Pristine+NP+NF” CFCCs. The standard deviation of the maximum load is given in parentheses.

Table 5.7: Four-point bending test results for “Pristine+NP+NF” specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>d (mm)</th>
<th>Load (N)</th>
<th>D (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine+NP+NF</td>
<td>1.28</td>
<td>4.74 (0.32)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

An increase in load handling was observed compared to the previous three cases. Also, due to nanoparticle’s solid state influence, CFCC test specimens experienced a slight decrease in deflection to failure. Table 5.8 reports calculated mechanical properties of the CFCCs reinforced with the combination of yttrium oxide nanoparticles and carbon nanotubes. Equations (1) thru (4) were utilized in a similar manner as described previously. Properties were averaged and standard deviations are given in parenthesis.
Table 5.8: Mechanical properties from 4-point bending test results for “Pristine+NP+NF” specimens.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Flexural Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Strain-to-failure (mm/mm)</th>
<th>Toughness (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine+NP+NF</td>
<td>45.03 (5.14)</td>
<td>53.80 (5.15)</td>
<td>0.000836</td>
<td>19.7 (2.86)</td>
</tr>
</tbody>
</table>

5.6. Discussions on the Comparison of the Results for Pristine and Nano-Reinforced CFCCs

The combination of 15wt% yttrium oxide nanoparticles and carbon nanotubes nanoforests proved to provide the highest flexural strength, modulus of elasticity, and toughness compared to CFCCs without any reinforcement and with only one type of nano reinforcement. Also, a slight decrease in strain to failure was observed compared to CFCCs reinforced with carbon nanotubes only. This phenomenon was due to the inclusion of nanoparticles within the matrix structure of CFCCs. However, “Pristine+NP+NF” still demonstrated a higher strain compared to “Pristine” and “Pristine+NP”. Table 5.9 reports the mechanical properties of all four types of CFCCs studied in this research.

Table 5.9: Compiled mechanical properties for all four types of CFCCs.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Flexural Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Strain-to-failure (mm/mm)</th>
<th>Toughness (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>32.83 (3.06)</td>
<td>45.5 (5.66)</td>
<td>0.000643</td>
<td>12.4 (2.70)</td>
</tr>
<tr>
<td>Pristine+NP</td>
<td>34.68 (4.06)</td>
<td>50.7 (3.80)</td>
<td>0.000573</td>
<td>13.3 (1.69)</td>
</tr>
<tr>
<td>Pristine+NF</td>
<td>41.99 (2.54)</td>
<td>47.78 (7.17)</td>
<td>0.000955</td>
<td>19.1 (5.35)</td>
</tr>
<tr>
<td>Pristine+NP+NF</td>
<td>45.03 (5.14)</td>
<td>53.80 (5.15)</td>
<td>0.000836</td>
<td>19.7 (2.86)</td>
</tr>
</tbody>
</table>
Figure 5.11 compares the Flexural strengths of all four types of CFCCs as listed in Table 5.9. Percentages of improvements in strength compared to the base “Pristine” CFCCs are given in Figure 5.11b.

![Graph showing Flexural strengths and improvements](image)

Figure 5.11: Flexural strength comparison for all four types of CFCCs. a) Flexural strengths in MPa, and b) percent improvements in flexural strength compared to “Pristine” CFCCs.

The highest flexural strength was demonstrated by CFCCs reinforced with both nanoparticles and carbon nanotubes. A 37% increase in flexural strength compared to the baseline CFCCs without any nano reinforcements was achieved. Figure 5.12a compares the toughness calculated for each type of CFCCs. Figure 5.12b demonstrates the percentages of improvements in toughness that were achieved compared to the baseline “Pristine” CFCCs.
Figure 5.12: Toughness comparison for all four types of CFCCs, a) Toughness in MJ/m², and b) Percent improvements in toughness compared to “Pristine” CFCCs.

An initial decrease in toughness was observed for CFCCs reinforced with nanoparticles only; however, a total increase of about 59% was achieved utilizing a combination of nanoparticles and carbon nanotubes as reinforcements. Figure 5.13a compares the values derived for modulus of elasticity for all four types of CFCCs studied in this work. Figure 5.13b demonstrates the percentages of improvements in modulus compared to baseline “Pristine” CFCCs.
Figure 5.13: Elastic moduli comparison for all four types of CFCCs, a) Elastic moduli in MPa, and b) Percent improvements in elastic moduli compared to “Pristine” CFCCs.

An increase of 18% in elastic modulus was achieved for combination reinforced CFCCs compared to the baseline “Pristine” CFCCs. Figure 5.14 compares the amount of strain the CFCCs underwent up to failure point.

Figure 5.14: Average strain to failure for all four types of CFCCs.
Similarly, Figure 5.15 shows the deformation to failure for all four types of CFCCs studied in this work.

![Graph showing deflection to failure for different CFCC types]

5.15: Average deflection to failure for all four types of CFCCs in mm.

It can be verified that a slight decrease in strain and deflection to failure is present due to the influence of nanoparticles.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1. Conclusions

Four different systems of continuous fiber ceramic composites (CFCCs), (i.e., Pristine, Pristine+NP, Pristine+NF, Pristine+NP+NF), are manufactured, following preceramic polymer pyrolysis (PIP) route. In this study, effects of different nano-materials on the flexural mechanical properties of continuous fiber ceramic composites (CFCCs) are experimentally investigated. Five different sets of CFCC specimens are manufactured and tested. Woven Silicon Carbide (Nicalon™) ceramic fabric is used here. Preceramic polymer (KiON CERASET®) is used as the base matrix in the current study. A characterization analysis of the samples using scanning electron microscopy reveals excellent quality of the manufactured parts. High carbon nanotube growth on ceramic fabric and good dispersion of yttrium oxide nanoparticles in matrix are obtained for all sets of samples, leading to excellent quality of the manufactured parts. Four-point bending test, based on ASTM C1341 standard, is conducted to evaluate the mechanical performance of the ceramic composite samples at room temperature. All the tested samples fractured inside the uniformly stressed region of flexure specimen (i.e., between the inner loading points of the fixture).

Initially continuous fiber ceramic composites without any reinforcements are manufactured. For these sets of samples named “Pristine”, neat preceramic polymer is used for all reinfiltration/pyrolysis cycles. Samples were then tested. After the initial results, three types of nano reinforced CFCCs (nanocomposites) are manufactured to be
compared with baseline “Pristine” CFCC. “Pristine+NP” depicts CFCC reinforced with 15wt% yttrium oxide nanoparticles, “Pristine+NF” depicts CFCC reinforced with carbon nanotube nanoforest, and consequently, “Pristine+NP+NF” depicts CFCCs reinforced with a combination of 15wt% yttrium oxide nanoparticles and carbon nanotube nanoforest. Nanoparticles (i.e., yttrium oxide) used in this work, varied in size from 15-55 nanometers. Carbon nanotubes employed in this study had lengths in the range of 30-50 nanometers. Plain weave ceramic fiber reinforcements (Nicalon™) woven fabric is used here. Preceramic polymer (KiON CERASET®) is mixed with the nano size particles in the presence of a surfactant agent to give a good dispersion of the particles during the process and is used as the matrix. A characterization analysis of the samples using scanning electron microscopy revealed excellent quality of the parts. In general, the weight gain percentage at each stage of reinfiltination/pyrolysis for both types of nanoparticle filled ceramic nanocomposites is consistently less than that for ceramic composites manufactured without nanoparticles. This shows the compactness of the nanocomposites. Four-point bending test is conducted to evaluate the flexural mechanical performance of the nano ceramic composite samples at room temperature. All the tested samples fractured inside the uniform loading region of flexure specimen (i.e., between the inner loading points of the fixture). As a result, CFCCs reinforced with a combination of nanoparticles and carbon nanotubes had the highest performance such as over 45% improvement in flexural strength, about 60% improvement in toughness, and over 18% improvement in modulus of elasticity compared to the baseline “Pristine” CFCC, achieved in this work.
Further, experimental results concluded that CFCCs reinforced with a combination of nanoparticles and carbon nanotubes, show consistently better flexural strength as well as toughness compared to their unreinforced CFCC counterpart. This result is a major breakthrough in the research area of 3D ceramic composites.

6.2. Future Work

There are a number of studies related to this work that are subject of future studies. For example, the structural (e.g., bending and tension) and non-structural (e.g., thermal, etc.) performances of the pristine and nano-reinforced materials should be evaluated at higher temperatures of 1500 to 1600 °C. In addition, it is important to evaluate the performances of various preceramic polymers at room - and high – temperatures for their pristine and nano-reinforced materials cases, and study the effects of pyrolysis temperatures of 1000 °C and 1500-1600 °C for the above-mentioned cases.

Finally, the characterization studies (e.g., SEM, TEM, etc.) should be conducted on the specimens during the preparation and as-manufactured specimens (for the study of the nanoparticle and carbon nanotube bondings to the matrix) as well as the fracture surfaces of the mechanically tested specimens to provide insights, in the quality control as well as fracture mechanisms of these advanced Continuous Fiber Ceramic Nano-composites (CFCNs).
REFERENCES


47. ASTM standard: C1341-97, Standard Test Method for Flexural Properties of