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## Synthesis, Processing and Characterization of Polymer Derived Ceramic Nanocomposite Coating Reinforced with Carbon Nanotube Preforms

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**SYNTHESIS, PROCESSING AND CHARACTERIZATION OF  
POLYMER DERIVED CERAMIC NANOCOMPOSITES COATING  
REINFORCED WITH CARBON NANOTUBE PREFORMS**

by

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B.S. Shanghai Maritime University, 2012

A thesis submitted in partial fulfillment of the requirements  
for the degree of Master of Science  
in the Department of Mechanical and Aerospace Engineering  
in the College of Engineering and Computer Sciences  
at the University of Central Florida  
Orlando, Florida

Summer Term

2014

Major Professor: Jihua Gou

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## **ABSTRACT**

Ceramics have a number of applications as coating material due to their high hardness, wear and corrosion resistance, and the ability to withstand high temperatures. Critical to the success of these materials is the effective heat transfer through a material to allow for heat diffusion or effective cooling, which is often limited by the low thermal conductivity of many ceramic materials. To meet the challenge of improving the thermal conductivity of ceramics without lowering their performance envelope, carbon nanotubes were selected to improve the mechanical properties and thermal dispersion ability due to its excellent mechanical properties and high thermal conductivity in axial direction. However, the enhancements are far lower than expectation resulting from limited carbon nanotube content in ceramic matrix composites and the lack of alignment. These problems can be overcome if ceramic coatings are reinforced by carbon nanotubes with good dispersion and alignment.

In this study, the well-dispersed and aligned carbon nanotubes preforms were achieved in the form of vertically aligned carbon nanotubes (VACNTs) and Buckypaper. Polymer derived ceramic (PDC) was selected as the matrix to fabricate carbon nanotube reinforced ceramic nanocomposites through resin curing and pyrolysis. The SEM images indicates the alignment of carbon nanotubes in the PDC nanocomposites. The mechanical and thermal properties of the PDC nanocomposites were characterized through Vickers hardness measurement and Thermogravimetric Analysis. The ideal anisotropic properties

of nanocomposites were confirmed by estimating the electrical conductivity in two orthogonal directions.

To my family

## **ACKNOWLEDGMENT**

I would like to thank Dr. Jihua Gou, my research advisor and the director of the Composite Materials and Structures Laboratory (CMSL) at UCF, who provided me with a great opportunity to access the world of nanocomposite materials, and this opportunity gave me a better understanding of composite material and trained myself to be a better researcher. He is an intelligent and energetic research professor, and his insight suggestions and sage counsel provide me a great deal of inspiration and motivation. I wish to express my appreciation to Donovan Lui who provided generous help and advice for my experiments. My appreciation also goes to Xin Wang, who shared knowledge of materials with me all the time. I would like to thank Dr. Fei Liang, whose advice on the adventures of graduate school is invaluable.

I would express my appreciation to my family. I would like to thank my loving parents, Zaiyuan Yang and Zihui Qiang, my sister Hongbi Yang and my brother in law Rongwei Yang for their patience and support in every level of my education. I would also like to thank my beloved Xiaolin for her constant support and confidence on me in all of the endeavors I have undertaken in each step of my career development. To them I humbly dedicate this work.

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# CHAPTER 1 INTRODUCTION

## 1.1 Motivation

Ceramic coating materials have drawn more attention than ever before in both academic research and industry manufacturing due to its excellent performance in high temperature and high stiffness with relatively low density. With those favorable properties, ceramic coating materials have been considered as a great thermal coating protection system candidate for gas turbine blade, air jet engine combustion shroud, atmospheric reentry vehicle and some other high temperature application. However, the brittleness of ceramics impedes its boarder usages as structural materials. This shortcoming has been greatly improved upon with the use of additives, among which, carbon nanotubes are particularly desirable as a reinforcement for ceramics due to its outstanding mechanical properties. The use of carbon nanotubes fillers is low cost and easy to conduct, but high content of carbon nanotube is hard to achieve due to the increased viscosity of the resin with the additives. Thus, limited improvement has been achieved with small amount of carbon nanotubes reinforcement.

The low thermal conductivity is another disadvantage of ceramics. Many high temperature components failure is caused by the heat concentration on some localized spots resulting from low thermal conductivity of ceramics. Therefore, increasing its thermal conductivity is necessary in order to meet the long-term durability requirements of high-temperature applications. Carbon nanotube has high thermal stability and remarkable thermal

conductivity in its axial direction, which in theory could reach up to 3000 W/m•K [1]. Therefore, carbon nanotubes could be considered to be one of the most promising reinforcement for this purpose. However, random carbon nanotube fillers reinforced composite could not fully take advantage of the highly anisotropic properties of carbon nanotube. The alignment of carbon nanotube is critical in order to reclaim this highly desirable property.

All above, the enhancement effect of carbon nanotube in ceramics matrix coating materials is limited if used as random fillers. In this study, instead of random fillers, we use carbon nanotubes as an aligned preform to increase the content of carbon nanotubes in nanocomposite and to form a known and preferably selective alignment, namely, vertically carbon nanotubes (VACNTs) and Buckypaper. Polymer derived ceramics (PDC) were selected to better take advantage of the high thermal conductivity of carbon nanotubes and the favorable heat-resistance of ceramics, because PDC is initially in liquid, which is ideal for composite manufacturing.

## **1.2 Research Method**

### 1.2.1 Anisotropic properties of materials

In order to better design the nanocomposites coating material, we need to understand the need of heat transfer within the nanocomposite. In general, there are two kinds of heat diffusion pathway needed. The first one is of high thermal conductivity in thickness direction, while it has low in-plane thermal conductivity. This kind of material could solve

the problem of low cooling efficiency in gas turbine blade or van if the heat transfer pathway is along thickness direction. The ability of heat dissipation could be used in microprocessors or integrated circuit packages to overcome the risk of damage resulting from the high power of the circuitry elements [10]. The other anisotropic material has an orthogonal heat pathway to the previous one. On one hand, the high in-plane thermal conductivity could enable the in-plane heat have a better distribution, therefore, the risk of localized hot spots decreases which is a very important feature to increase the durability of high temperature applications. On the other hand, the low thermal conductivity in thickness direction serves as insulation to protect the substrate. This nanocomposites could be served as thermal barrier coating materials.

### 1.2.2 Objective

With a limited research achievement being done with the improvement to thermal properties and behavior of ceramic, the objective of this thesis is to synthesis, process and characterize a new ceramic nanocomposite. Previous work within the research group has shown that the addition of a carbon nanofibers, nanotubes, and other fillers can improve the thermal behavior of a composite significantly [2-5]. This leads to a novel idea of using different carbon nanotube preforms as heat transfer pathway in ceramic matrix nanocomposites. As a rule of thumb, desirable nanocomposite that could be able to protect the underlying substrate should, in one hand, have a selective pathway of heat dissipation and on the other hand, have a low thermal conductivity in another desired direction. Simultaneously, intrinsic thermal stability, high mechanical performance, good corrosion and low density should be achieved.

This thesis demonstrated the advantages of using carbon nanotube preforms, namely VACNTs, Buckypaper and fuzzy fibers, over carbon nanotube random fillers as reinforcement in regarding increase of carbon nanotube content, mechanical properties improvement and highly anisotropic properties.

### **1.3 Structure of the thesis**

The main body of this thesis from Chapter 2 to Chapter 6 is organized by the following structure. Chapter 2 reviews some background of carbon nanotube, and the research on ceramic matrix composites using carbon nanotube as reinforcements. The physical properties, operation processing of polymer derived ceramics has been cover in this chapter as well. Base on the characters of carbon nanotube and ceramics, as well as the recent research development, three carbon nanotube preforms, namely VACNT, Buckypaper and fuzzy fibers, are proposed and characterized under scanning electron microscope in Chapter 3. Then, the discussion focus in Chapter 4 is the processing of carbon nanotube preforms and polymer derived ceramic. In Chapter 5, the manufactured materials, were then tested for thermal stability using a TGA. The anisotropic electrical conductivity is confirmed by electrical conductivity estimation in plane and through thickness direction. Mechanical properties of nanocomposite is characterized by hardness measurement. The thesis concludes in Chapter 6 with a summary of the achievement and future work planned to expand the data available on this new material, including the mechanical properties, thermal properties, and optimization of the manufacturing process.



## **CHAPTER 2 LITERATURE REVIEW**

### **2.1 Carbon Nanotube reinforced nanocomposite**

Carbon nanotubes are under radar in the last two decades due to their superior properties. Theoretical and experimental studies have proved that carbon nanotubes have remarkable mechanical properties [6-9]. The axial thermal conductivity of CNTs was estimated at room temperature can reach up to 3000 W/m•K [10]. Besides excellent high thermal conductivity, the thermal stability of CNTs is impressive as well. The thermal stability of CNT is estimated to be up to 2800°C in vacuum and 750°C in air [11]. With these outstanding properties, CNTs are considered to be a great candidate as nanofillers which could be used to produce high-performance ceramic nanocomposite with multifunctional properties. Many research groups have investigated the mechanical properties enhanced by adding carbon nanotube into composites [12-15]. There are three major mechanical properties improvement mechanisms have been concluded: (1) The crack deflection, (2) Crack-bridging, (3) CNT pull-out [16, 17]. Adding CNTs could not only fabric stronger and tougher ceramics, but also could increase the electrical and thermal conductivity of ceramics [55-58]. Since CNT possesses anisotropic properties, it naturally motivate researchers to fabric anisotropic materials by using CNTs as reinforcing elements. Recent study has shown that the thermal conductivity of CNT/Ceramic nanocomposites exhibits different thermal behaviors in different directions [10]. This makes potential materials for applications as thermal barrier layers in microelectronic devices, gas turbine blade and vanes, and so on.

### 2.1.1 VACNT reinforced composites

The growth of CNTs has been developed over 30 years since their discovery, several approaches have been used, including arc discharge, laser-vaporization, and chemical vapor deposition. [18-22] Chemical vapor deposition (CVD) stands apart among these production methods for its ease of use and low cost. CVD also holds a special advantage in that it can be performed with a wider variety of substrates, even in-situ with other materials, such as ceramics. [23] The inherent ability to grow aligned CNT “forests” has been exploited for the highly anisotropic properties.[24] Li, et al have shown the effects that the choice of the precursor has on the CNTs grown by CVD. [25] Castro, et al have studies the influence of the thermal gradient within the reactor on the rate of formation of catalyst and CNTs. [26] The effect of catalyst in VACNTs has been studied by Sato et al. as well. [27]

The CNTs are densely packed while retaining the intrinsic properties of CNTs, such as high surface area, flexibility and thermal conductivity. This leads many researchers to have a depth investigation on utilizing VACNTs as reinforcement. For example, Fan, S. and his group fabricate thermal interfacial material combining VACNTs and epoxy, whose thermal conductivity could reach up to  $6.5 \text{ Wm}^{-1}\text{K}^{-1}$ . [28] Robert Cross et al. developed a  $130\mu\text{m}$  thick thermal interface material by bonding VACNTs to metallized substrates which showed low thermal resistances as low as  $10\text{mm}^2\text{kw}^{-1}$ . [29] Thermal conductivity of VACNTs has been estimated using a modern light flash device by Shaikh and colleagues. [30] However, polymer matrix, used in the majority of research, could only tolerant low

temperature range, therefore, we seek an alternative to take place of polymer in order to achieve high temperature application. Polymer derived ceramics has high temperature stability, high chemical resistance could be a great candidate matrix for VACNTs. This will be discussed in later sectors.

### 2.1.2 Buckypaper reinforced composites

The CNT Buckypaper, is a paper-like CNT film. It can be prepared by pressure chamber filtration or vacuum filtration of CNT dispersion or made of aligned carbon nanotubes by “domino pushing”, typically presents thermal conductivity around a couple of hundreds of  $Wm^{-1}K^{-1}$  in plane direction and low thermal conductivity in thickness direction [31-34]. This feature could be used to remove the localized hot spots in high temperature loading condition. Many research are focus on polymer matrix reinforced by Buckypaper [35-37], therefore, the composite can only be used at ambient and mild temperatures. To fulfill the high temperature application, ceramics with high melting temperature, low density and superior corrosion resistance is considered in this research.

## **2.2 Polymer Derived Ceramic**

Polymer derived ceramics (PDCs) represent inorganic/organometallic materials convert from polymer molecules to ceramics by proper thermal treatment (curing and pyrolysis processes) under a controlled atmosphere. The development of pre-ceramic polymers to produce near-net shapes in a way not known from other techniques [38]. PDCs have drawn many research interest since its emergence for the following advantages: near net shape forming, low process cost, and the ability to achieve homogeneous enforcing elements distribution at molecular level [39-42]. There are a few groups of PDCs, and the

oversimplified general formula is presented in Figure 1 [43]. The variation of (X) results in different classes of Si-based polymers such as polysilanes with X = Si, polycarbosilanes with X = CH<sub>2</sub>, polysiloxanes with X = O, and polysilazanes with X = NH. Typical polymer precursors commonly used include polycarbosilane (PCS), polysiloxane (PSO), and polysilazane (PSZ), producing amorphous Si-C, Si-O-Si and Si-C-N ceramics respectively upon pyrolysis.

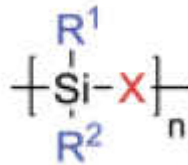


Figure 1 General simplified ceramic precursor formula

In the 1958, Kumada et al. reported the method to synthesis of PCS [44], and then Yajima and his colleagues made a significant progress and presented SiC ceramic materials by the pyrolysis of polycarbosilanes [45, 46]. Now several ceramic precursors are commercially available due to its high ceramic yield and some other advantages.

The processing of ceramic precursors could be divided into 4 segments including: 1) Shaping, 2) Polymer cross-linking, 3) Polymer-to-Ceramic conversion, 4) Ceramic crystallization. In each segment, the precursor undergoes different chemical reactions, oligomer evaporate and gas release at different temperatures, see in Figure 2. This process involves the initial cross-linking of polymer precursors followed by a thermal induced polymer to ceramic transformation by removing the polymer chains and leaving the

ceramic backbone. Major drawbacks of PDCs are large weight loss and shrinkage of ceramics during pyrolysis.

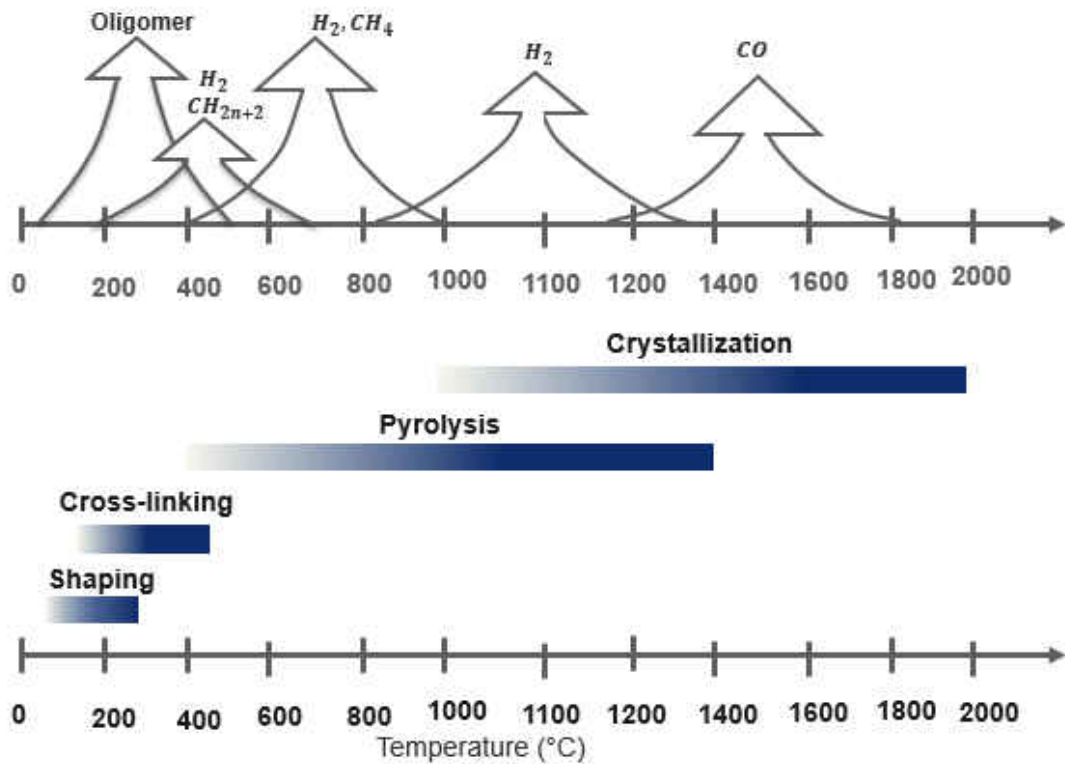


Figure 2 Polymer to Ceramic transformation

### 2.3 Carbon Nanotube preform reinforced Ceramic nanocomposite

Ceramics are generally of low electrical conductivity and thermal conductivity. To improve its conductivity, conductive fillers are added into ceramics in the forms of fibers, yarns, mats, pellets and powder.[47-50] Most of researches using carbon nanotube as reinforcement, and properties are enhances from different aspects, such as mechanical properties, conductivity, and so on. [50, 51, 54] Despite the remarkable properties of CNTs, the reinforcing effect of CNTs in ceramics is far below the expectation. There are three

problems that needed to be solved: 1) inhomogeneous dispersion of CNTs within the ceramic matrix, 2) Inadequate densification of the composites, 3) poor wetting behavior between CNTs and the matrix [12]. These drive researchers looking for some other novel methods are proposed for instance: Higginbotham, Amanda L., et al use 30-40 W power input microwave to cure the PDCs with 0.75% load of CNTs, and the temperature could reach 1150°C in 7 minutes [52].

## CHAPTER 3 CARBON NANOTUBE PREFORMS

### 3.1 VACNT Array

#### 3.1.1 CNTs growth mechanism

CNT growth mechanisms has been debated since its discovery in 1991 [18]. However, no single CNT growth mechanism is recognized by all researchers. Nevertheless, one of theories is widely accepted, which can be outlined as follows. The hydrocarbon firstly decomposes into carbon and hydrogen when it contact with metal catalyst at elevated temperature. Then, carbon would dissolved in metal nanoparticle. This process keeps happening until the carbon content reaches the carbon-solubility of the metal at that temperature. Then, the as-dissolved carbon precipitated out and crystallizes. Since the network of carbon is in cylindrical, it has no dangling bonds and hence it is in energetically stable. The CNT growth process ceases once the metal is saturate with carbon, its catalytic function stops and so does the CNT growth [59].

#### 3.1.2 VACNT Growth

In our case, VACNTs were grown using a CVD process as described in the literature review. The schematic figure of CVD setup is shown in Figure 3.

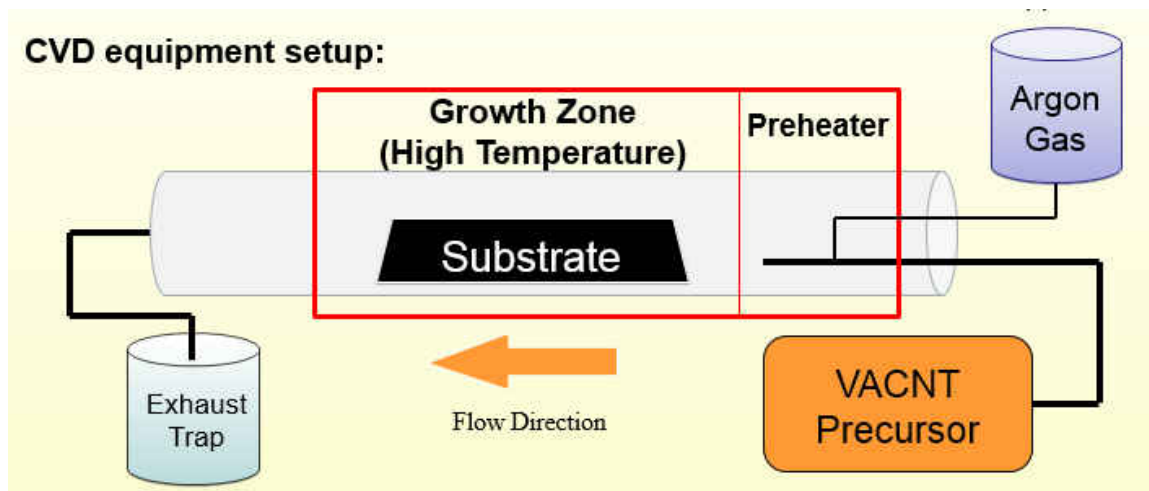


Figure 3 Schematic figure of CVD equipment setup

This process was carried out using a precursor mixture composed of Ferrocene and Toluene. Ferrocene (Sigma-Aldrich, MO) is an organometallic compound with the formula  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , which is bright orange powder. It serves as catalyst in the CVD process, because it generates nanosize Fe particles at elevated temperature and become the basement of CNT growth.

Toluene is clear, water-insoluble liquid with boiling temperature of 111 °C, serving as carbon source. Ferrocene was dissolved in toluene with the composition of 97.5% toluene and 2.5% ferrocene by mass. After adequately mixing, a reasonable amount of precursor could be transferred into a syringe which would be mounted on a programmable syringe pump. The CVD assembly is seen Figure 4



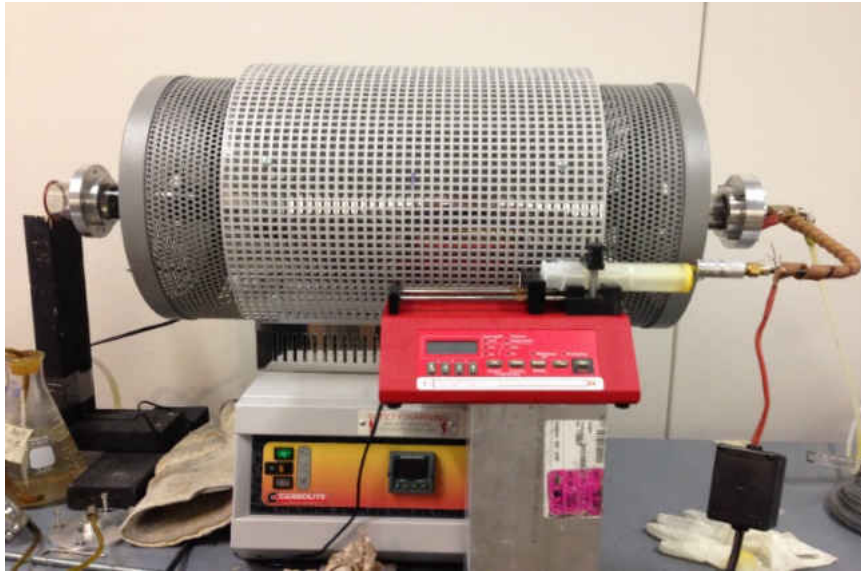


Figure 4 VACNT Manufacturing Configuration

The injection rate of syringe was set to 10 mL/hour, and 20 mL of VACNT precursor was used in each run, and the growth duration was set as 2 hours at 750 °C for our application purpose. Evaporation temperature of toluene was only of 111 °C, in each process we could preheat the precursor above this temperature, so that the mixture would be evaporated into the tube. The preheat process is very important because the gas phase of precursor would largely improve the uniformness of distribution. The temperature cycle of tube furnace was set as shown in Figure 5.

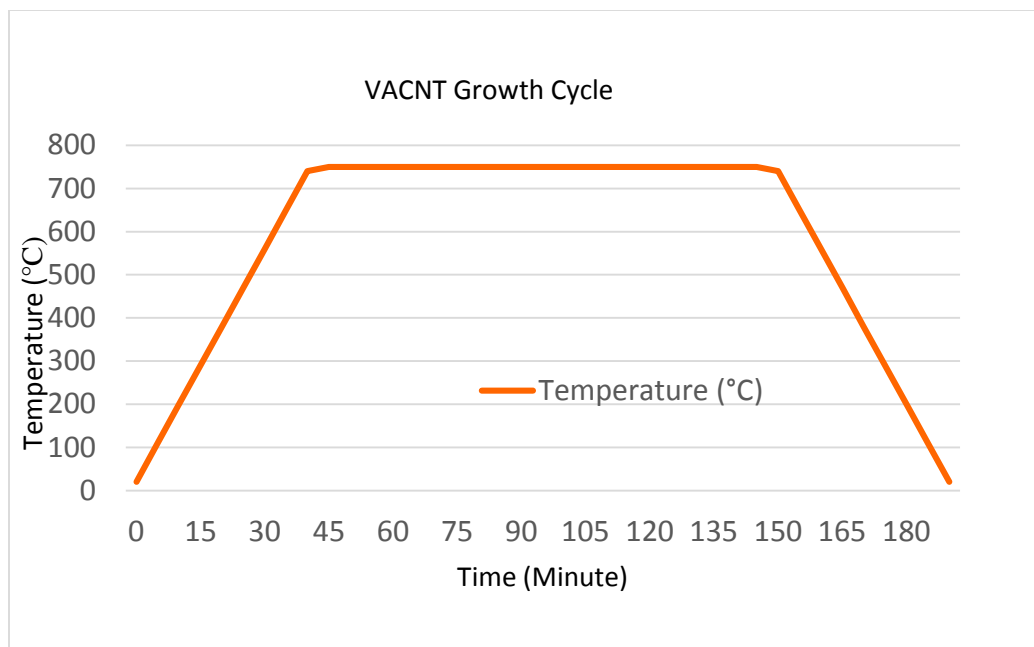


Figure 5 VACNT temperature cycle chart

Then, the VACNT precursor would be carried by a stable argon flow (2 L/min) in the reactor. Argon flow does not produce any pressure, yet only the inert atmosphere is necessary. The tube was flushed with argon until the furnace temperature cool down below 300°C following the growth phase to prevent CNT from oxidation.

This process produces a uniform array of VACNTs on the surface of the quartz substrate (See Figure 6), but also yields a large amount of CNTs on the surface of the reactor (quartz tube) walls. These CNTs, as with the VACNTs on the surface of the quartz substrate, always grow normal to the tube walls. These CNTs are the byproduct of VACNTs growth which could be used as fillers or in nanopaper fabrication.

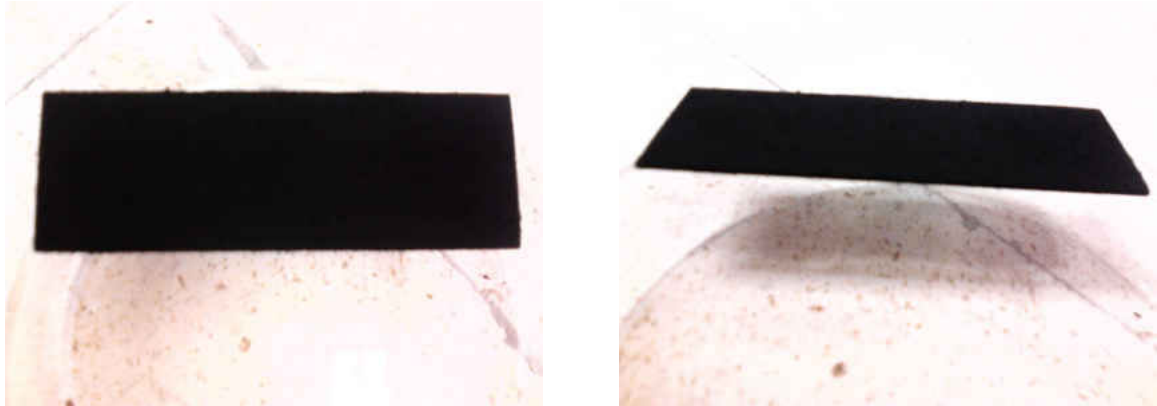


Figure 6 (a) Top view of VACNT array (b) Side view of VACNT array

CNTs grow perpendicular to substrate because the array is so dense that CNT pushes each other, and thus the only direction for them to form cylindrical structure is upward.

### 3.1.3 Morphology of VACNT

Aligned arrays were fabricated using chemical vapor deposition method. Morphology of the VACNT was shown by Scanning Electron Microscope (SEM). Dense VACNTs array could be observed with good uniformity. The average height is approximately 600  $\mu\text{m}$  estimated from the cross section view (Figure 7).

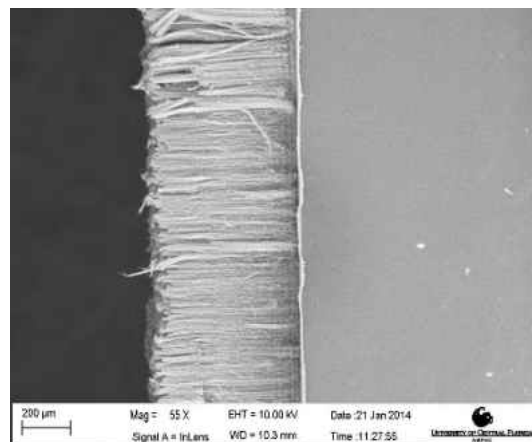


Figure 7 Cross-section of VACNTs array

It should be noted that the height of VACNTs array is controllable and we could achieve the VACNTs forest of 1.25 mm height, which is observable with naked eyes. As can be seen in Figure 8, the VACNTs array is detached from the substrate and the root portion is disordered resulting from the removal process. However, the upper part of VACNTs forest keeps its straight growth configuration and the uniformity retains. The estimated height is 1.25 mm, and this achieved by using higher growth temperature (850°C). It is notable that the control of VACNTs height is not accurate, but it provides us a valuable factor that affects the quality of VACNTs growth.

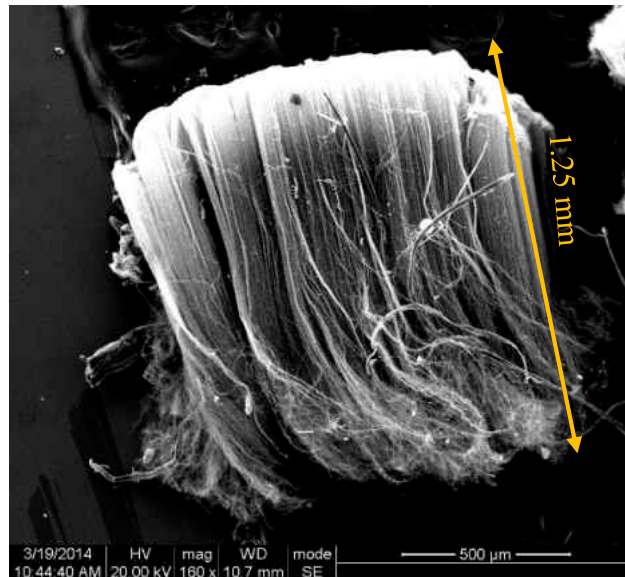


Figure 8 Cross-section of detached VACNT array

More detailed VACNTs array SEM image is illustrated in Figure 9. Consistent diameter of CNTs throughout the height could be observed. The diameter of representative CNT is around 150 nm.

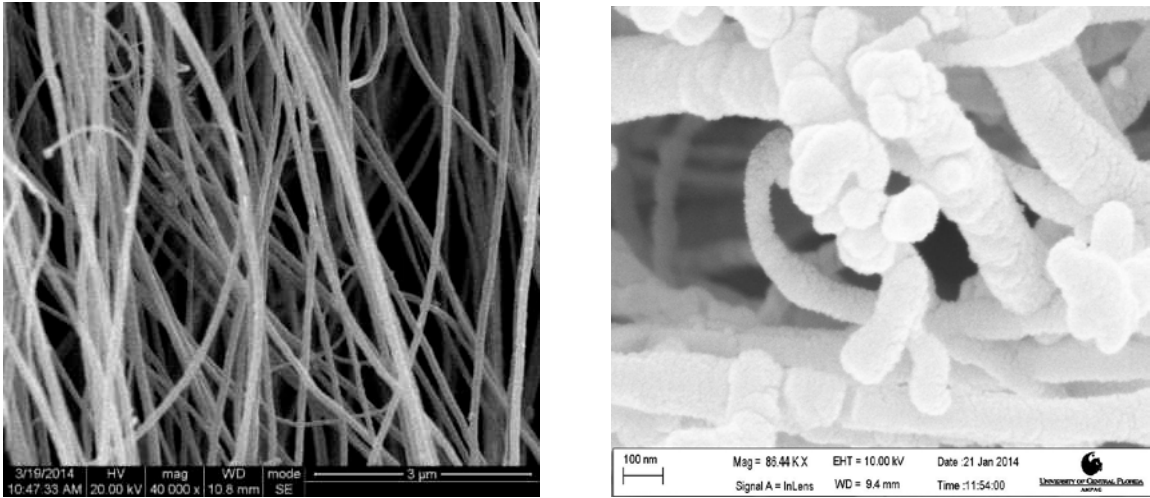


Figure 9 High magnification SEM images of CNTs

### 3.2 Buckypaper

As stated in the previous chapters, the purpose of fabricating the Buckypaper/Ceramic nanocomposite coating material onto the surface of a substrate is to take advantage of its in-plane high thermal conductivity to avoid localized hot spots, as well as its low thermal conductivity through thickness direction to insulate the surfaces of components from high temperature thermal load. This highly anisotropic functional coating material has potential applications in many industries, such as thermal coating system of atmosphere reentry vehicle and refractory materials.

To fabricate carbon nanotube buckypaper, the carbon nanotubes were purchased from commercial company, CNano Technology (Zhenjiang) Ltd., China. The as-received carbon nanotubes were dispersed in 1000 ml distilled water with the aid of surfactant Triton-X100 (10 drops per 1000ml). The mixture was sonicated for an hour under 1500

watts power input. It should be pointed out that the more input power during the sonication process, the better dispersion quality could be obtained. However, carbon nanotube could be damaged if the input power was too strong or the sonication duration was too long. After the sonication process, the well dispersed suspension will be filtered through a hydrophilic filter (Millipore, MA) with the pore size of  $0.45\mu\text{m}$  using pressure assistant filtration system (Figure 10). The suspension was poured into a pressure chamber right after sonication in order to keep its good mixing. The pressure was used to compress the excessive water penetrating the filter and leaving carbon nanotubes on the filter. The pressure used to assist filtration process was 100 psi. After the filtration, a diameter of 110 mm and 1 mm thick buckypaper could be peeled off from the filter and could be dried in air or in open oven.

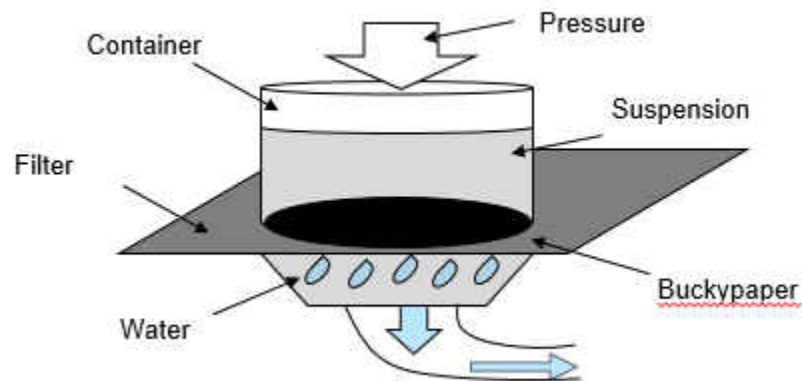


Figure 10 Schematic of pressure assistant infiltration system

The quality of the Buckypaper made by the pressure assistant infiltration system is shown in 11. The thickness is uniform and the surface is very smooth.

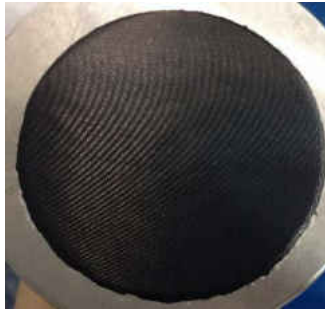


Figure 11 Buckypaper

### **3.3 Fuzzy Fiber**

Another carbon nanotube preform that we could extend from carbon nanotube growth is fuzzy fiber [60, 61]. Since the VACNTs were grown via floating catalyst chemical vapor deposition (VCCVD), catalyst is filled in the whole space of reactor. Inspired from carbon nanotube growth on the sidewall of quartz tube, the growth process should happen on any substrate as long as the substrate material has the ability to survive at 750°C.

Continuous long fiber reinforcements are dominant in composite industry. However, the interface between fiber and matrix is somewhat weak in many cases, which negatively affect its mechanical properties. Not only that, the lack of interlayer bonding is another shortcoming, and this usually cause delamination under heavy load [62, 63]. In order to overcome these two challenges, modification of fiber surface is an option. As stated earlier, as long as the fiber could keep intact above 750°C, the carbon nanotube could grow on fibers using FCCVD.

In this study, we used alumina ceramic fibers as our fuzzy fiber substrate, which is suitable for high temperature application. The operating temperature and melting temperature of ceramic fibers are 1200°C and 1800°C respectively, therefore, it qualifies the temperature requirement. The temperature cycle of carbon nanotube growth on ceramic fibers is identical to that of VACNTs, and the shiny light color fibers turn into black dark fibers after the CNTs growth process (See Figure 12).



Figure 12 (a) Ceramic fibers before CNTs growth (b) Fuzzy ceramic fibers

SEM micrographs of CNTs grown on the bunch of carbon fibers are shown in Figure 13. It can be seen that a uniform anchoring of CNTs on ceramic fibers indicating that fiber surface equally attractive growth surface like quartz. It should be noted that the CNTs growth in some area are better than another. This is because the fibers are bundle together tightly on some part of surface, and these covered surfaces have no contact with catalyst as



well as carbon source. But overall, the bundle of fibers are covered with a great amount of CNTs (See Figure 14).

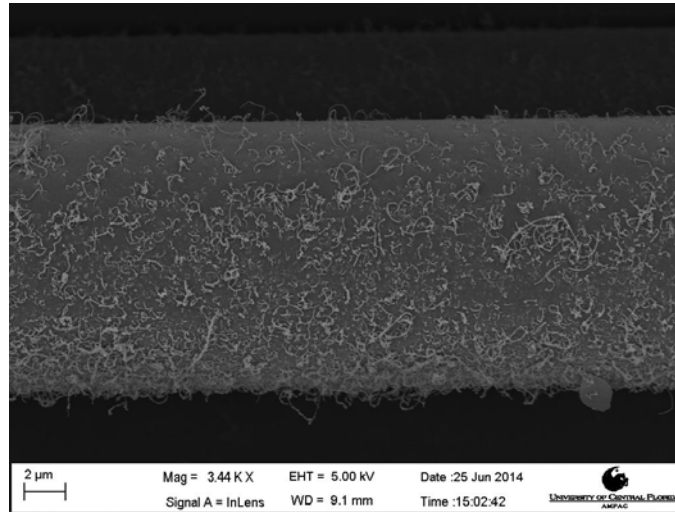


Figure 13 SEM image of individual fuzzy fiber

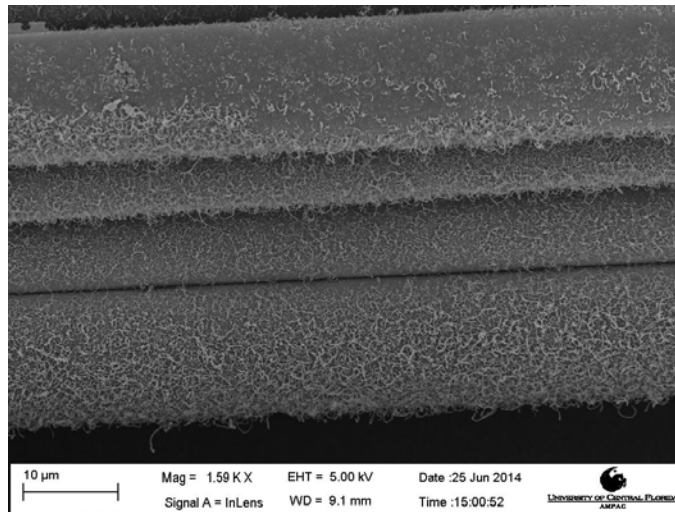


Figure 14 SEM image of fuzzy fibers

## CHAPTER 4 SYNTHESIS OF POLYMER DERIVED CERAMIC NANOCOMPOSITES COATING REINFORCED WITH CARBON NANOTUBE PREFORMS

### 4.1 Two types of ceramic precursors

The ceramic matrix precursors we used were liquid polymers with low viscosity. It has many advantages, such as ease of use and near net shape manufacture. There are types of ceramic precursors we use – polysiloxane and polycarbosilane, and the detailed comparisons are shown in Table 1. Both these two ceramic precursors have high ceramic yields, high thermal stability and high purity.

Table 1 Two types of ceramic precursors

	<b>Polysiloxane</b>	<b>Polycarbosilane</b>
<b>Denotation</b>	SPR-688/SPR-212	SMP-10
<b>Operating temperature</b>	1100°C	1800°C
<b>Density</b>	1.11 $g/cm^3$	0.998 $g/cm^3$
<b>Catalyst</b>	Platinum CAT-776	Dicumyl Peroxide and toluene mixed

The ceramic precursors convert into ceramics via three major temperature cycles, namely soft curing cycle, hard curing cycle (polymer cross-link) and pyrolysis cycle. The flow chart is shown in Figure 15.

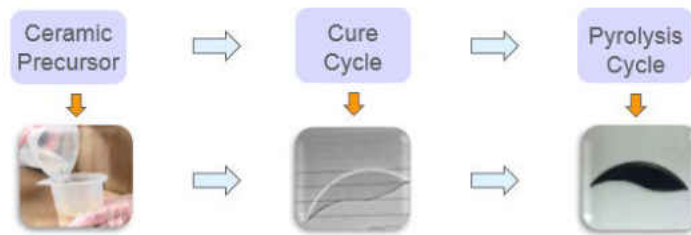


Figure 15 Chart flow of curing and pyrolysis

The soft curing cycle is shape forming process. The liquid polymer turns into clear glass-like solid in a mold at a relatively low temperature with the present of catalyst. The soft cycle is very temperature sensitive, therefore the temperature ramp has to be controlled with caution. If the gradient of temperature is too high, crack will occur due to residual thermal stress. After the shape had formed, the part was put into oven without any molds or tooling at a higher temperature. The Hard curing cycle is less temperature sensitive, and used to fully crosslink the polymer matrix in preparation for the pyrolysis process. The pyrolytic conversion of the polymer precursor into the ceramic final product is carried out under an inert, argon atmosphere, and is carefully controlled to prevent any damage to the siloxane ceramic matrix as the volatile compounds pyrolyze. The results of the pyrolysis is a fully formed siloxane ceramic matrix that has a relatively high volumetric shrinkage during pyrolysis, but can be reinfiltreated to decrease any voids that form as a result of the conversion. The detailed temperature cycles for polysiloxane and polycarbosilane are shown in Table 2 and Table 3.

Table 2 Temperature cycles for polysiloxane

<b>Cycles</b>	<b>Temperature</b>	<b>Condition</b>	<b>Atmosphere</b>
<b>Soft curing</b>	RT-80°C	Ramp Heat at 3°C/min	Atmospheric
	80°C	Hold for 60 min	
	80°C-RT	Cool down at 3°C/min	
<b>Hard curing</b>	RT-200°C	Ramp Heat at 5°C/min	Atmospheric
	200°C	Hold for 120 min	
	200°C-RT	Cool down at 5°C/min	
<b>Pyrolysis</b>	RT-650°C	Ramp Heat at 1°C/min	Inert; Argon positive flow; atmospheric
	650°C-750°C	Ramp Heat at 2°C/min	
	750°C	Hold for 120 min	
	750°C-RT	Cool down at 5°C/min	

Table 3 Temperature cycles for polycarbosilane

<b>Cycles</b>	<b>Temperature</b>	<b>Condition</b>	<b>Atmosphere</b>
<b>Soft curing</b>	RT-100°C	Ramp Heat at 3°C/min	Atmospheric
	100°C	Hold for 60 min	
	100°C-RT	Cool down at 3°C/min	
<b>Hard curing</b>	RT-250°C	Ramp Heat at 5°C/min	Atmospheric
	250°C	Hold for 120 min	
	250°C-RT	Cool down at 5°C/min	
<b>Pyrolysis</b>	RT-650°C	Ramp Heat at 1°C/min	Inert; Argon positive flow; atmospheric
	650°C-850°C	Ramp Heat at 2°C/min	
	850°C	Hold for 120 min	
	550°C-RT	Cool down at 5°C/min	

## 4.2 VACNT/Ceramic

The matrix resin preparation was easy and straightforward. Ceramic precursor resin and catalyst were thoroughly mixed with a ratio of 49:1 by mass using a high-speed centrifuge machine. Degassing process was also conducted in order to achieve voids free resin. The VACNTs preform stands on quartz substrate, and then, the mixture was poured on the VACNTs preforms. The resin could penetrate the preform easily due to the effect of capillary force of VACNTs forest array. After hand layup process, the samples were put into a vacuum chamber for 30 minutes for further resin penetration in order to remove the air bubbles trapped inside the nanocomposite. In the vacuum chamber, the layer of air bubbles, arising from bottom of nanocomposite, would form about 2 minutes after vacuum was introduced. After this process, infiltration was conducted again. In order to obtain a dense composite, above processes were repeated for 3-4 times, and less air bubble could be observed after each process cycle. Excessive pure resin could be observed on the top of nanocomposite, which could cause curvature after pyrolysis.

Then, the nanocomposite samples were cured and pyrolyzed according to the temperature cycles of ceramic precursors. The nanocomposite could get off from substrate after soft cure cycle. The schematic of manufacturing process is shown in Figure 16.

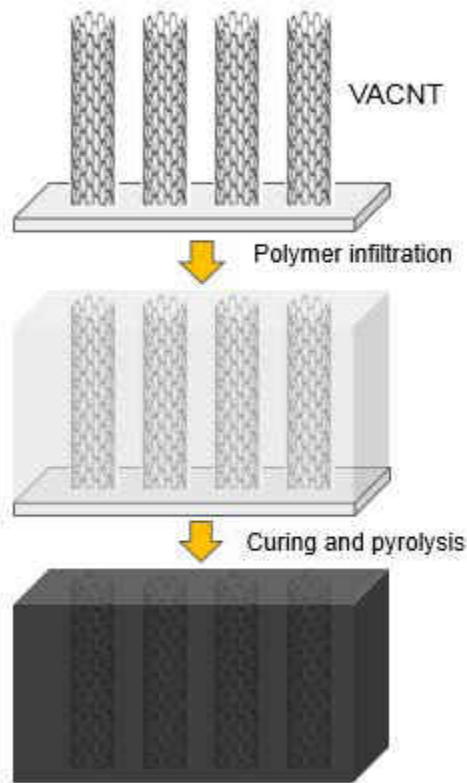


Figure 16 Schematic of VACNT/Ceramic nanocomposite manufacturing process

### 4.3 Buckypaper/Ceramic

In order to fabric dense Buckypaper/Ceramic nanocomposite, the most widely used bagging technique was used with pressure and vacuum in autoclave. The layout of the tooling design is shown in Figure 17. A release agent was spread on the tooling surface to ensure that the nanocomposite part could be removed from tooling without damage the Buckypaper/Ceramic coating film. Then, a release film that has a slightly larger size was placed on top of release agent thin film. The ceramic precursor was evenly brushed on the release film. After reasonable amount of precursors covering the release film, a Buckypaper was placed on it, and the preloaded resin underneath the Buckypaper would

prevent Buckypaper from sliding and the bottom of Buckypaper would be fully immersed into precursor. Then, more precursor was hand layup on Buckypaper until it had a good impregnation. Another release film was covered on the preform before being bagged by a clear membrane. The clear membrane was tapped on the tooling via double-sided high temperature tape with good sealing. In the whole soft curing process, a 15 psi pressure and 20 inHg vacuum was used in autoclave, see Figure 18. Using pressure and vacuum have two major advantages: 1) Making stronger interface between reinforcement and matrix, 2) Removing excessive polymer, which could avoid curvature during pyrolysis process.

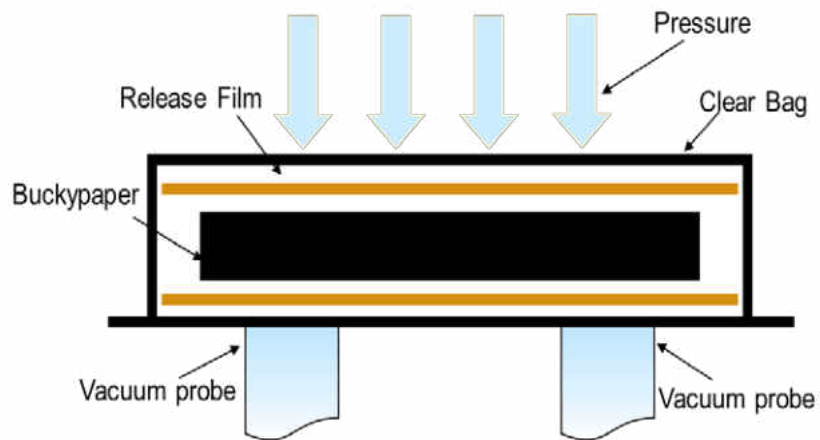


Figure 17 Schematic of bagging technique



Figure 18 Autoclave tooling

The Buckypaper/Ceramic samples in shown in Figure 19. After pyrolysis, the shrinkage in-plane is 20.5% for both length and width direction. The mass fraction of carbon nanotube is 26.1%, and 46.6% of volume fraction was achieved. The density of Buckypaper/Ceramic samples is  $2.32g/cm^3$ .

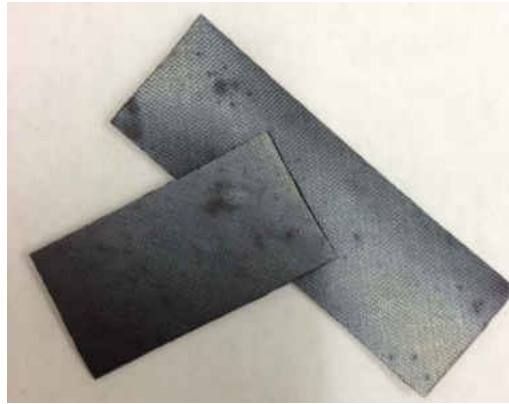


Figure 19 Buckypaper/Ceramic nanocomposites



## **CHAPTER 5 CHARACTERIZATION AND TESTING**

Scanning electronic microscope was used to observe the microstructure of VACNT/Ceramic and Buckypaper/Ceramics nanocomposite. The thermal stability of nanocomposite was tested by a thermogravimetric analyzer (TA Instruments Q5000 IR) with sample weight of 40 mg to characterize its thermal stability.

In order to reveal the anisotropic properties of carbon nanotube preforms reinforced ceramic nanocomposite, the electrical resistivity were measured in two orthogonal directions, namely in-plane and through thickness. The in-plane electrical resistivity of both VACNT nanocomposites and buckypaper nanocomposites were measured with a four-point apparatus (Signatone Quadpro System). The electrical resistivity through thickness was measured using Volt-Ampere law. The samples were painted with silver glue on both sides of sample. The DC power supply (MASTECH HY3005D) was used, the maximum voltage is 30 V. Additionally, the mechanical properties were characterized via hardness measurement.

### **5.1 Scanning Electron Microscopy**

Aligned arrays were fabricated using floating catalyst chemical vapor deposition method. The microstructure was observed using Zeiss ULTRA-55 FEG SEM. The configuration of

VACNT was retained and the alignment was still observable in nanocomposite. The thickness of nanocomposite is about 1mm, see Figure 20.

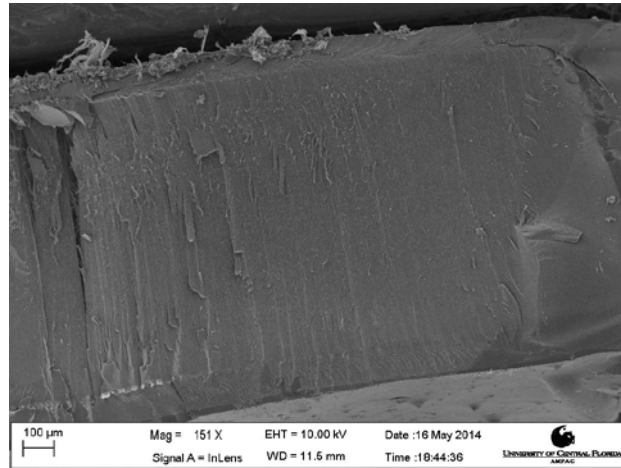


Figure 20 Cross-section of VACNT/Ceramic before pyrolysis

Good bonding between carbon nanotube and ceramic could be observed in Figure 21. The carbon nanotubes were covered by ceramics, which could provide good mechanical properties.

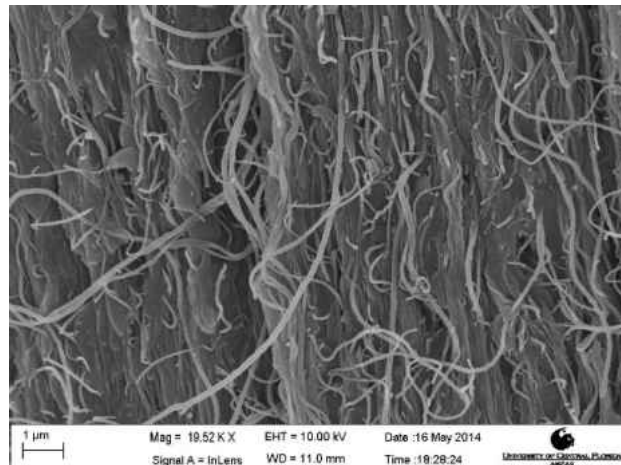


Figure 21 High magnification of VACNT/Ceramic

In Figure 22(a), it shows a very interesting phenomenon that cracks developed after ceramic pyrolysis, and the majority of cracks are perpendicular to the axis of carbon nanotube. The crack propagation is perpendicular to carbon nanotube could be observed in Buckypaper/Ceramic nanocomposite as well, and the only difference is that the crack is patterned in-plane instead of in the cross-section in VACNT/Ceramic nanocomposite. Even with the presence of crack and porosity, the nanocomposite comes in a whole unit. This is because the cracks are bridged by carbon nanotubes, and this phenomenon could be observed in Figure 22(b).

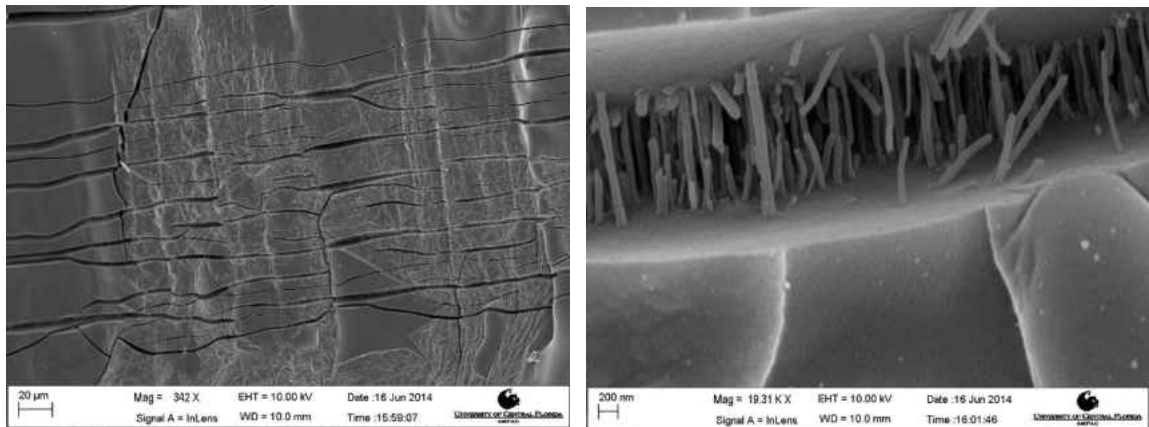


Figure 22 (a) Crack in VACNT/Ceramic (b) Carbon nanotube bridging

The Buckypaper/Ceramic nanocomposite was fabricated using bagging technique. All the carbon nanotube are well dispersed, and no agglomeration could be found (Figure 23).

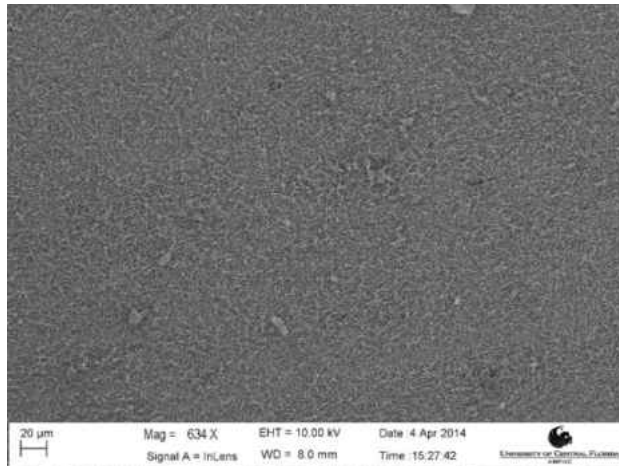


Figure 23 Buckypaper/Ceramic surface

As stated in the previous section, the crack developed during high temperature pyrolysis could be found in SEM images. The crack propagations have curtain pattern in-plane, and all the cracks are perpendicular to carbon nanotube alignment (See Figure 24). However, no crack could be found on the cross section surface. This feature could suggest that majority of carbon nanotubes are distributed in transverse plane. The crack pattern looks like an orthogonal network, which indicates that the assumption of uniformly distributed carbon nanotube in-plane is solid. The factors causing crack formation is still under investigation, but here we propose possibilities: 1) The evaporation of oligomer and gas release 2) The thermal residual stress developed during pyrolysis 3) The large shrinkage of during conversion from polymer to ceramic. Again, owing to carbon nanotubes bridging, the sample could be a complete piece nanocomposite even with the present of many micro cracks.

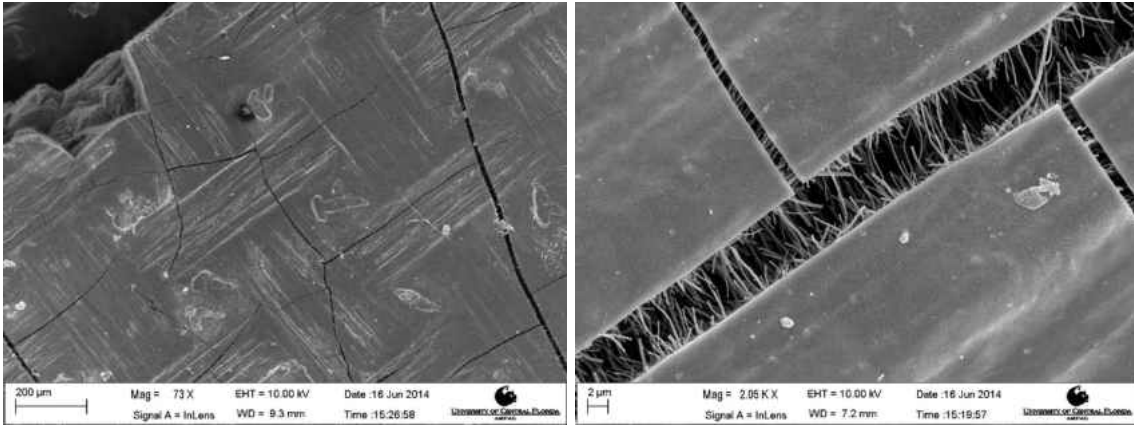


Figure 24 (a) Crack pattern on top surface of Buckypaper/Ceramic (b) High magnification fracture surface of Buckypaper/Ceramic

## 5.2 Thermogravimetric Analysis (TGA)

The thermal stability of samples was tested by a thermogravimetric analyzer in argon atmosphere with a temperature rate at 10 °C/min. The result indicates its high thermal stability, as can be seen in figure 25. In thermogravimetric figure, there is a relative high weight loss at round 98 °C, this is due to the moisture (water vapor) evaporation. After that, the weight is very stable and no additional mass loss at temperature from 200 °C to 640 °C. Then, the first stage of decomposition is expected because starting at 640 °C, the weight starting decrease at a relatively higher rate. However, when the temperature reaches 700 °C, 99.75% of mass still remains. Therefore, a good thermal stability of VACNT/ceramics composite coating materials was obtained.

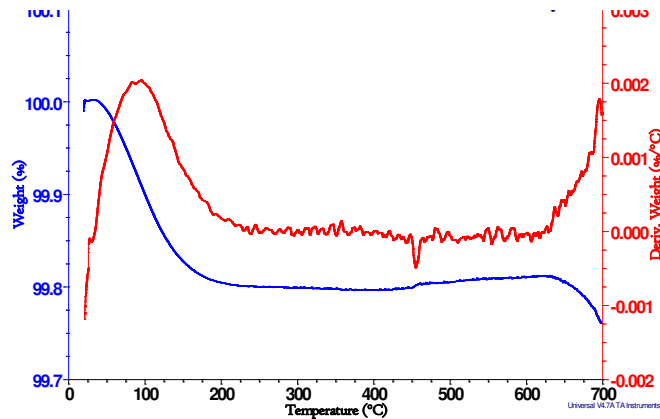


Figure 25 Thermogravimetric analysis of VACNT/Ceramic

## 5.3 Electrical Conductivity

### 5.3.1 In-plane

The electrical conductivity of both VACNT/Ceramic and Buckypaper/Ceramic nanocomposites were measured with a four-point probe apparatus, which consisted of a combination of four probes in a straight line with a constant inter-probe spacing (S) of 1.56 mm. Figure 26 shows a schematic representation of rectangular sample preparation for conductivity measurements. Uniformly distributed five points were selected, and on each spot, two perpendicular directions of electrical conductivity were measured. The in-plane electrical conductivity of VACNT/Ceramic sample could not be measured due to its large resistivity. However, the Buckypaper/Ceramic nanocomposite sample shows a much better conductivity. Both sides of Buckypaper/Ceramic nanocomposite were conducted conductivity measurements and the results are shown in Figure 27. For the rough surface, the fifth point has a large resistance, which could be due to the excessive ceramic layer covering that spot. After excluding the fifth spot on the rough surface, the resistivity is consistent on

both sides. For the smooth, the resistivity is around 65Ω·cm while that of rough surface is about 58 Ω·cm.

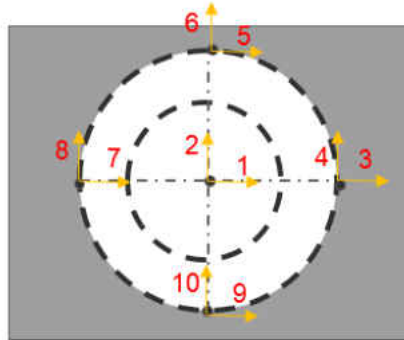


Figure 26 Schematic representation of sampling points

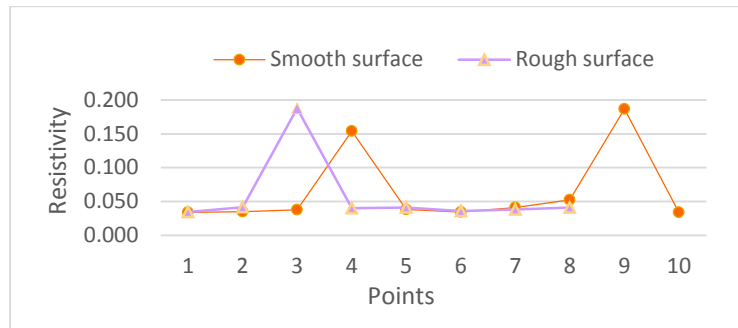


Figure 27 Electrical conductivity of sampling points on both sides of sample.

### 5.3.2 Through thickness

All the samples are painted with silver glue on both sides in order to avoid contact resistance. A linear relationship between voltage and ampere could be seen in Figure 29. According to the resistance, the dimension of samples and the paint area, the electrical conductivity could be calculated by the following equation:

$$\sigma = \frac{L}{RA}$$

Where,  $L$  is the thickness of sample;  $A$  represents the area of silver painting area, and  $R$  is the resistance of the sample. The electrical conductivity of Buckypaper/Ceramic could not be measured due to its large resistance through thickness direction. While that of VACNT/Ceramic is  $80.1 \text{ s/m}$ , which indicates highly anisotropic properties of two different carbon nanotube preforms reinforced ceramic.

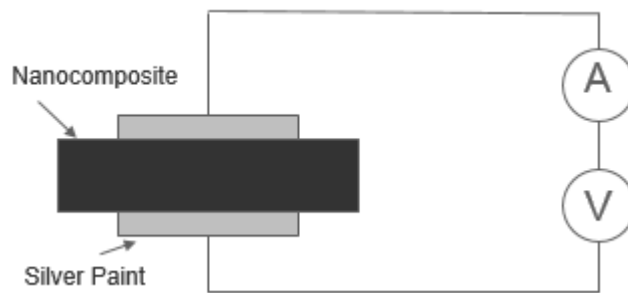


Figure 28 Schematic Resistance measurement device

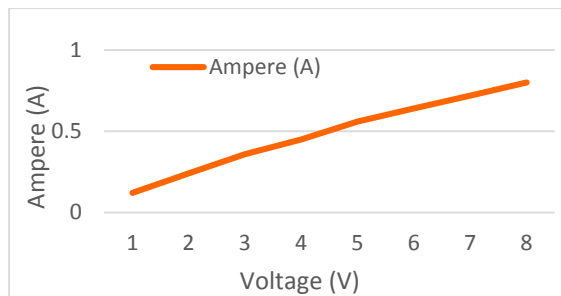


Figure 29 Voltage-Ampere characteristic figure

#### 5.4 Hardness measurement

The hardness measurements were performed on a LECO Vickers Hardness Tester LV 700 using ASTM C1327-08 standard for advanced ceramic material under HV1/15 (1 Kg load, and the dwell is 15 seconds) loading condition [53].



The testing samples were firstly immersed in liquid phase epoxy resin for sample preparation purpose. After epoxy fully cured, the surface was polished using 600 grit sandpaper in order to make sure the sample surface was exposed, flat and smooth (See Figure 30).

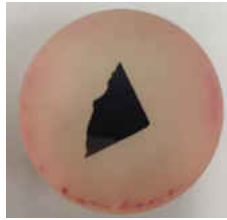


Figure 30 Prepared hardness measurement sample

The hardness could be estimated using the equation as follows:

$$HV = 0.0018544 \left( \frac{P}{d^2} \right),$$

Where P = load, N

d = average length of the two diagonals of the indentation, mm

The length of diagonals could be measured using the indentation images, and calculated from the standard equation. Alternately, the hardness could be read direction from the Vickers hardness tester by using the built-in microscope right above the sample fixture.

One VACNT/Ceramic sample, two Buckypaper/Ceramic composite from the same part but different sides and pure ceramic sample were measured. One side of Buckypaper/Ceramic nanocomposite has more excessive ceramic than another due to the manufacture process.

The hardness measurement is conducted on 10 isolated points on each sample, and 5 preferably indentations are used in calculation. The hardness results could be seen in table 4.

Table 4 Hardness results

<b>Samples</b>	<b>Hardness (GPa)</b>
Buckypaper + SMP-10	1.9
Buckypaper + SMP-10 (more PDC)	2.5
VACNT + SPR-688	1.85
Pure SPR-688	8.5

The pure ceramic has hardness of 8.5 GPa, while the hardness of ceramic decreases after reinforced by carbon nanotube preforms. The hardness of VACNT/Ceramic is lower than that of Buckypaper/Ceramic is unexpected because the load is in the carbon nanotube axial direction which should have the improvement. However, the porosity and crack in nanocomposite introduced by VACNTs is dominated, which could be noticed in SEM. For Buckypaper/Ceramic, no hardness promotion is achieved because the load direction is in transverse direction of carbon nanotube, in which there is no hardness enhancement.

## CHAPTER 6 CONCLUSION AND FUTURE WORK

This thesis proposed three carbon nanotube preforms for different application purposes, including VACNTs, Buckypaper, and fuzzy fibers. There are three major advantages over random carbon nanotube fillers via those preform: 1) Increase the content of carbon nanotube within the composite, 2) An alternative way to avoid the agglomeration of carbon nanotube, 3) Anisotropic properties of nanocomposite coating materials with alignment.

The VACNTs growth was processed using FCCVD method, and the alignment was confirmed with SEM analysis. The height of VACNT array is controllable and the height range is from 5 $\mu$ m to 1300 $\mu$ m. This led us to use ceramic fiber as substrate to fabric fuzzy fibers that have potential to possess a better performance in mechanical properties and thermal and electrical conductivity than neat fiber reinforcement. Buckypaper was fabricated using pressure assistant infiltration system, and its ability to conduct heat at a lower rate in thickness direction than in-plane direction is important to dissipate heat to avoid localized hot spots or to insulate the surface of substrate from high temperature loading condition.

The high thermal stability of carbon nanotube preform reinforced ceramic matrix composite was proved using Thermogravimetric analysis, which suggests its availability for high temperature applications. An electrical conductivity of VACNT/Ceramic through thickness of 6.6 s/m was measured, yet the in-plane electrical resistant was too large to

estimate. The similar phenomenon has been observed in Buckypaper/Ceramic, on the plane which is dominated by uniformly distributed carbon nanotube in plane, electrical conductivity is of 0.161 s/m, but in the direction perpendicular to the plane, the electrical resistance is too large to measure. The anisotropic electrical conductivity has been shown, which could potentially predict that the thermal conductivity would vary in different direction as well.

Mechanical properties of carbon nanotube preforms reinforced ceramic nanocomposite was estimated via hardness measurement. The results along with scanning electronic microscopic images suggest that crack and porosity has been developed within the nanocomposite after pyrolysis.

All the work have done leads us to next investigation in future work. Firstly, the detachment of carbon nanotube from substrate is needed, otherwise, the mismatch thermal expansion coefficients between matrix and substrate would cause residual stress within the body, which is considered to be one of the major factor inducing cracks in nanocomposite. Besides, injection mold technique is necessary in PDC cure cycle due to the large shrinkage, which could help further dense the nanocomposite by consistent PDC resin feeding. Polymer infiltration and pyrolysis (PIP) would be conducted in order to avoid the crack and voids in nanocomposites.

Thermal conductivity in different directions needs to be measured to further confirm its anisotropic character and functionality of carbon nanotube preforms reinforced ceramic nanocomposite. Additionally, higher temperature thermal stability could be studied to exploit its better performance.

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