

Organosilicon polymer-derived ceramic fibers: Fabrication and molecular
structure investigations

by

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B.S., Qingdao University of Science and Technology, 2014

M.S., Oregon State University, 2016

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

DOCTOR OF PHILOSOPHY

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KANSAS STATE UNIVERSITY
Manhattan, Kansas

2020

Abstract

As humans entered 21st century, the energy crisis has gained more attention and reached a critical situation that may impede the further innovation of science and technology. Along with the development of the Internet and wireless communication, electronic devices, from automated production robots down to small consumer electronics, are overtaking our lives at a rate that none of the conventional industries can compete with. This leads to the ever-growing demand for energy production, transportation, and storage. In addition to the investigations on clean or renewable energy sources, more researches are promoting the efficiency of generating or utilizing the already existed forms of energy.

Aerospace related development and applications consume a significant amount of resources. As a critical unit of aerospace application, turbine engines may be effectively advanced by the reliable high-temperature components in not only the performance but the efficiency. Fiber-reinforced ceramic matrix composites (FRCMCs) are proposed as the next-gen material of turbine high-temperature components (such as turbine blades, shrouds, combustor liner, exhaust nozzle, etc.), with high oxidation and creep resistance and outstanding mechanical performance at elevated temperatures but lower density than single crystals. Within the CMCs, ceramic fibers serve as the major performance support.

Polymer derived ceramics (PDCs) or polymer derived ceramic route is an innovated ceramic production technique, developed over the last half-century, that begins with the synthesis or the selection of monomer molecules (therefore also known as molecular methods); fine-tunes at the precursor stage; shapes during crosslinking stage; and converts the organic components into inorganic ceramics via pyrolysis. This method enables the synthesis of uniform ceramic fibers at a much lower temperature and easier processing condition than conventional powder-based synthesis. PDC fibers (SiC, Al₂O₃, BN, etc.) have already shown great potential in high-temperature applications as reinforcement of CMCs.

This thesis focus on the synthesis and characterization of ceramic fibers from silicon-based liquid-phase precursors. The fibers are drawn using two different techniques (hand spinning and electrospinning), that are able to deliver individual ceramic fibers and ceramic fiber mats. The first approach demonstrates the preparation of SiOCN fibers from a hybrid precursor of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasilazane (referred to as TTCSZ) and polyacrylic acid (PAA) using hand spinning. Later, SiOC fiber mats are synthesized via electrospinning from various cyclic preceramic oligomers or monomers with polyvinylpyrrolidone (PVP) as a spinning reagent. The fiber products are systematically investigated molecular structures, performances, and chemical bonding progression of the fibers at each processing stage (spinning, crosslinking, and pyrolysis).

The approaches for ceramic fiber spinning and pyrolysis processes utilize cyclic siloxanes and silazanes for the first time as the ceramic precursors that are low cost and available in large quantities. The products show great potential in high-temperature applications as well as other applications such as energy storage.

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Gurpreet Singh

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Dedication

This dissertation is dedicated to all my families and friends who supported me physically and mentally.

Chapter 1

Introduction

1.1 Background and Motivation

Aerospace propulsion systems such as gas turbine engines are crucial for commercial and military applications. In fact, more than 200,000 units of aircraft engines totaling more than \$ 1 trillion are expected to be sold through 2028¹, and \$ 2 trillion worth of engines are expected to be sold by 2031². However, rising concerns about the economic and ecological effects of storage and transportation activities have highlighted the importance of improved process efficiencies.

The energy efficiency of any heat engine is directly related to its working temperature³; a high working temperature reduces NO_x or CO emissions^{4;5}. Consequently, improved thermal efficiency requires turbine blades, the turbine vane, combustor liner, and exhaust nozzle to withstand a high inlet temperature^{4;5}. However, a high thermal and oxidizing working environment means the material must maintain high mechanical properties (strength and elasticity) as well as resistance to creep and corrosion at high-temperatures for the entire service period (up to thousands of hours)³. Operating cost, density of the selected material, and the number of load cycles⁶ are also taken into account³.

Metallic materials (single- or poly-crystalline metals or superalloys) with environmental barrier coating (EBC) and temperature barrier coating (TBC) have commonly been used

for heat turbine engines². However, metallic materials are limited by a sharp decrease in mechanical and chemical properties once the environment approaches the melting temperature of the metals. At the end of the 20th century, pushing the working temperature beyond 1500 °C could lower the gas turbine fuel consumption by up to 15 % from the previous generation³.

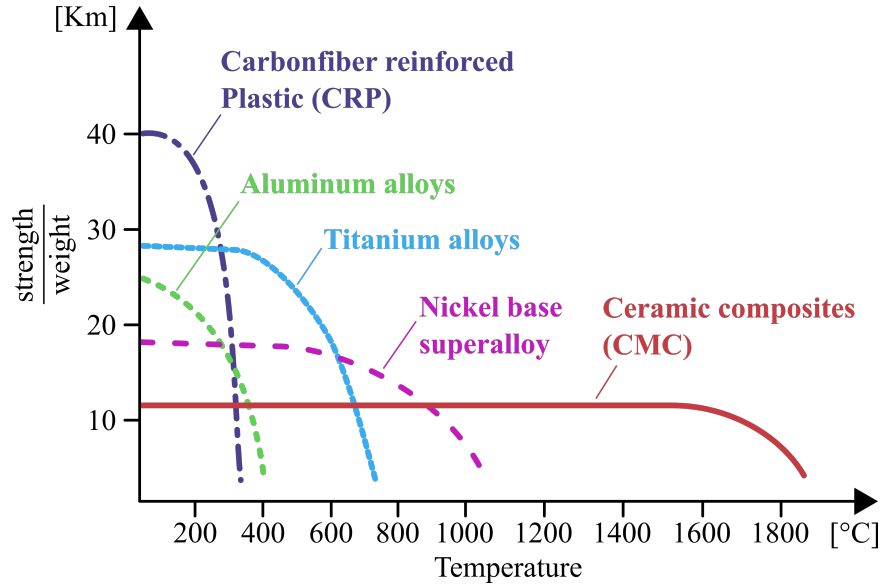


Figure 1.1: *Strength to weight ratio of different high-temperature materials vs temperature. Apparently, CMCs are able to maintain mechanical performance at elevated temperature (above 1500 °C) than other materials.*

Conversely, ceramic materials are broadly known for their outstanding mechanical performance (such as strength, modulus, low thermal conductivity⁷, hardness), efficient resistance to oxidation and corrosion, and superior stability at elevated temperatures⁸. However, inherent mechanical properties of the monolithic ceramic materials, specifically brittleness (or low fracture toughness) that lowers the reliability, have limited their application to structural applications^{3;8}. Unlike metals that exhibit significant plastic deformation by dislocations, ceramics are very sensitive to cracklike defects that are initiated during both manufacturing or functioning and quickly propagates without impedance^{3;7}. Two approaches can be used to improve ceramic toughness³: (1) increase the quality of the components by controlling the number and size of microstructural defects; (2) convert ceramics into composites with reinforcement. Years of research of CMC materials have shown that a favorable rein-

forcement of CMCs can greatly improve the toughness of the bulk ceramic phase. Other approaches have utilized three-dimensional (3D) micro/nano particulates, two-dimensional (2D) nanocoatings/sheets, or one-dimensional (1D) fibers/whiskers, as well as materials with unique compositions such as carbon-based materials (carbon fibers, graphene, carbon nanotubes), ceramic-based oxides (SiOC, Al_2O_3) or non-oxides (SiC, BN)⁹.

To fulfill the intense demand for ultra-high-temperature materials (Figure 1.1⁶), one of the approaches proposed for ceramic-based materials is to develop fiber-reinforced ceramic matrix composite (FRCMC) structures³. In the late 1970s, Yajima et al. showed how high-temperature ceramic fibers could be made from certain organometallic oligomers or silicon-based polymers using a combination of polymer and ceramic processing methods¹⁰. These high-temperature fibers demonstrated good mechanical properties, thermal properties, and oxidation resistance, and could be woven into textiles to make complex-shaped ceramic parts. These SiC fibers are the backbone of the ceramic-fiber ceramic-matrix technology for next-generation turbine engines (Figure 1.2¹¹)¹².

The synthesization of ceramic fibers from diverse molecular structures is known as a polymer derived ceramic (PDC) approach¹³. PDCs have gained extensive attention for their excellent properties (even surpassing conventional ceramics) such as high mechanical strength (Young's modulus of (150 ± 10) GPa, Vickers hardness of 25 – 27 GPa), elevated electrical conductivity ($6 \times 10^{-3} \text{ S cm}^{-1}$), remarkable thermostability, and resistance to corrosion and creep^{14;15}. The final properties of the PDCs can also be very effectively modified by tailoring the processing parameters¹⁶.

1.2 Liturature Review

1.2.1 High-temperature ceramics

Ceramics, which are generally nonmetallic, inorganic solid materials, were some of the first artificial materials or products used more than 9000 years ago¹⁷. Initially utilized as structural materials, ceramics are now used as functional, high-temperature materials in many

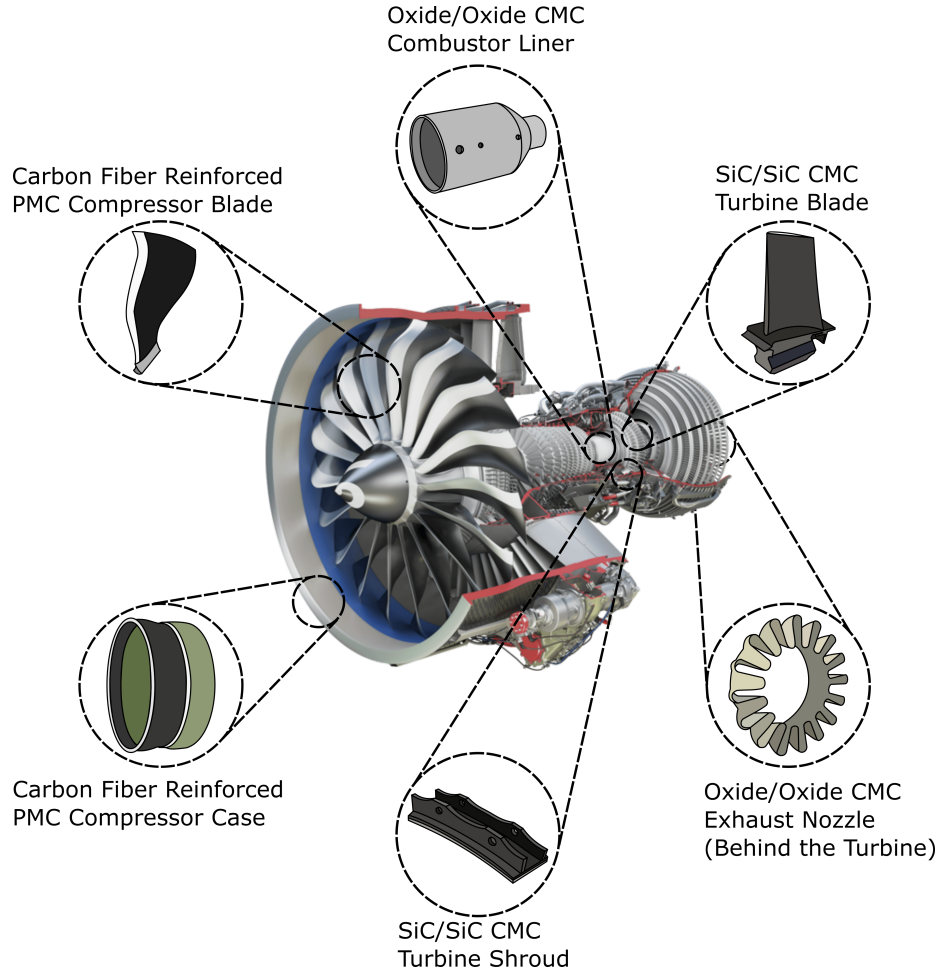


Figure 1.2: *Schematics of a gas turbine engine and high-temperature composites made of CMCs or PMCs with corresponding materials marked out.*

advanced applications for technology industries. Conventionally, advanced ceramics are high-technology ceramics with optimized composition, morphology, and properties (mechanical, chemical, thermal, or electrical) via densifying decent powders under properly controlled conditions. Advanced ceramic compounds are usually comprised of IIIA, IVA elements or transition metals (Ti, Zr, Mo, W) with light elements, such as B, C, N, O¹⁷. The wide varieties of ceramic compounds yield various bonding types (covalent, metallic, ionic, or mixed), therefore, adjustable physical and chemical properties^{18;19}. Due to the abundance of C, N, O, and Si in the earth's crust, these ceramics are economically and environmentally beneficial¹⁷.

Advanced ceramics have wide applications as structural materials due to their advan-

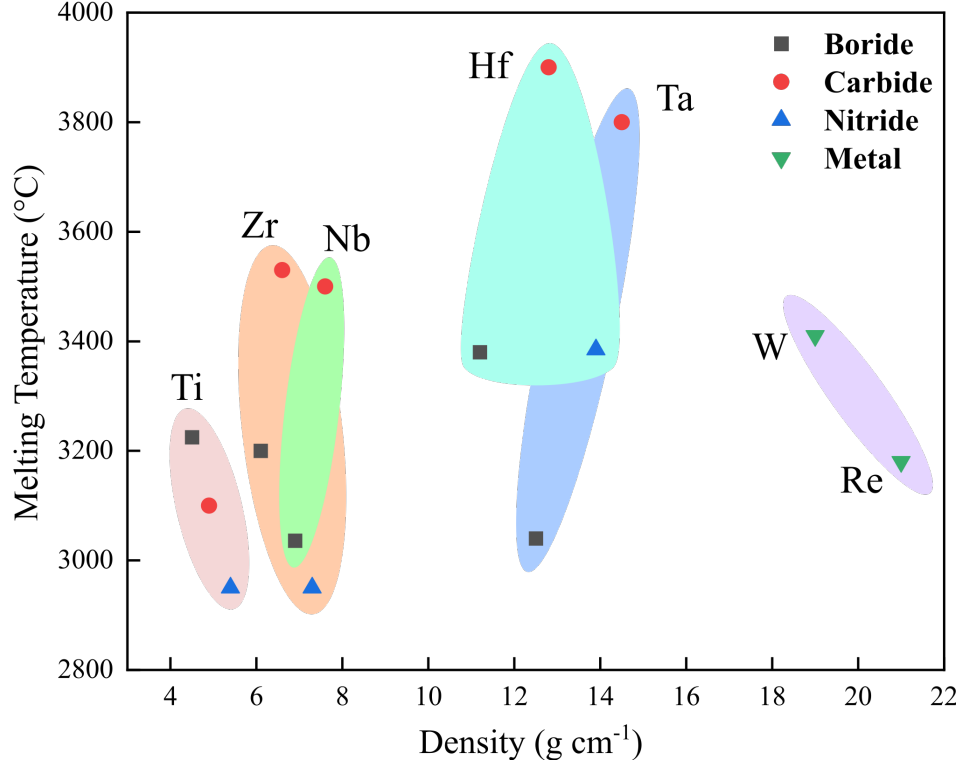


Figure 1.3: *Melting temperature vs density of UHTCs and metals. UHTCs can have comparable or superior melting temperatures than metals with much lower (as low as a quarter) densities.*

tageous physical and chemical properties, including beneficial mechanical properties (high strength, high modulus, high hardness, low density), and effective resistance to wear, creep, thermal and corrosion. Advanced ceramics also show potential as functional materials because of their attractive thermal, electrical, magnetic, and optical properties. Powder-based ceramics, however, have a covalent or ionic bonding nature, which induces brittleness and the poor reproducibility of the properties due to the complicated synthesis, shaping, and sintering of fine powders. Ultra-high-temperature ceramics (UHTCs) have a melting/decomposition point over 3000 °C that provides a working temperature greater than 2000 °C (Figure 1.3²⁰). Common engineering properties of UHTCs, as compiled by Golla, et al., are listed in Table.1²⁰.

Table 1.1: *Engineering Properties of UHTCs*

Material	Melting point (°C)	Density (g cm ⁻³)	Elastic modulus (GPa)	Hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})	Crystal structure
Carbide							
HfC	3900	12.8	300-340	26	250-350		FCC
TaC	3800	14.5	470-540	14-19	600-700	3.4	FCC
ZrC	3530	6.6	480	27	400		FCC
NbC	3500	7.6	338	20			FCC
TiC	3100	4.9	451				FCC
Nitrides							
HfN	3385	13.9	420		290-350		FCC
ZrN	2950	7.3	380		330		FCC
TiN	2950	5.4					FCC
Borides							
HfB ₂	3380	11.2	480	21-28	350-450		HCP
TiB ₂	3225	4.5	500-560	25-35	700-1000	4-5	HCP
ZrB ₂	3200	6.1	340-500	20-25	300-400	4	HCP
TaB ₂	3040	12.5	248-551	20-25	555	4.5	HCP
NbB ₂	3036	6.9	637	21	414	4	HCP

1.2.2 Polymer-derived Ceramics

The PDC approach is an advanced ceramic manufacturing technique based on the idea of designing the product molecular structure and properties from molecular or even atomic level¹⁸. To achieve this, the selection and synthesis of preceramic polymer precursors are essential. The wide agreed realization of the PDC concept dates back to the early 1960s when Ainger and Herbert reported first prepared a phosphorus nitrogen compound from a molecular precursor¹³ and Veerbeek and Winter prepared the first silicon-based PDC (Si₃N₄ and SiC). Subsequent researches benefitted from the innovation of organic chemistry synthe-

sizing techniques to synthesize precursors to convert to ceramics. As shown in Figure 1.4, PDC-related researches and corresponding literature have increased since 2010.

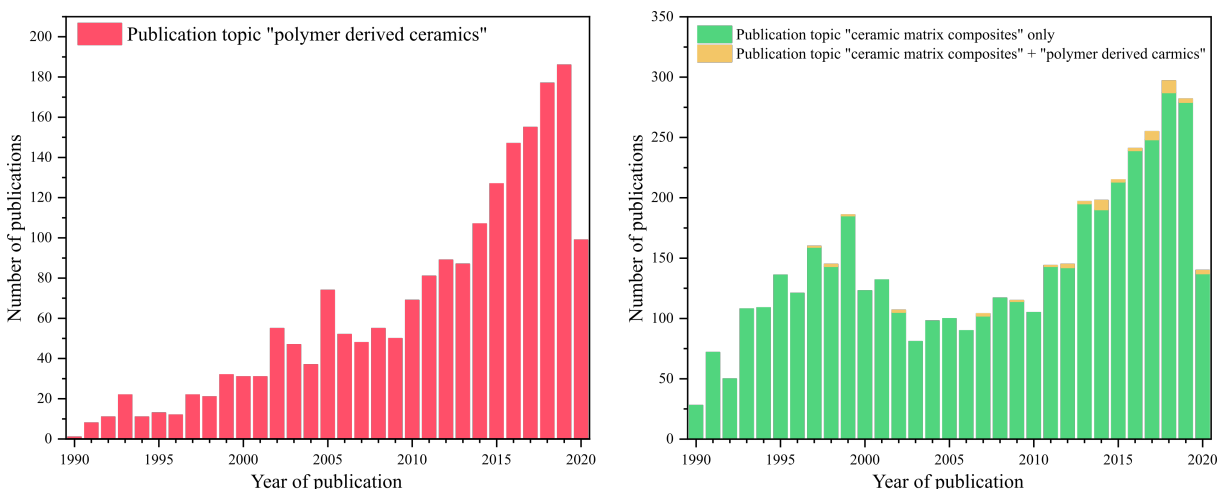


Figure 1.4: 30 years of publications focused on “polymer derived ceramics” (left) and “ceramic matrix composites” (right), from 1990 to June 2020. The numbers are obtained from ISI web of science.

The PDC technique includes the following steps (as shown in Figure 1.5) to synthesize silicon-based ceramics¹⁷:

1. Precursor preparation: synthesis of silicon-based polymers (silicon at the backbone) or oligomers from monomer (silicon compounds).
2. Crosslinking: formation of 3D network structures from 1-D or 2-D precursors via heat-treating at mild temperatures.
3. Polymer-to-ceramic conversion: the organic-to-inorganic transformation of network structures at elevated temperatures in protection environments - results in amorphous covalent ceramics.
4. Crystallization: phase transformation of amorphous ceramics into crystalline structures at a temperature greater than 1400 °C.

This technique can produce high-purity amorphous or crystalline ceramics at decreased heat-treatment temperatures compared to conventional powder sintering.

PDCs are unique¹³ because amorphous ceramics are achievable via other ceramic synthesis techniques (i.e. powder sintering or CVD); the polymeric network structures result

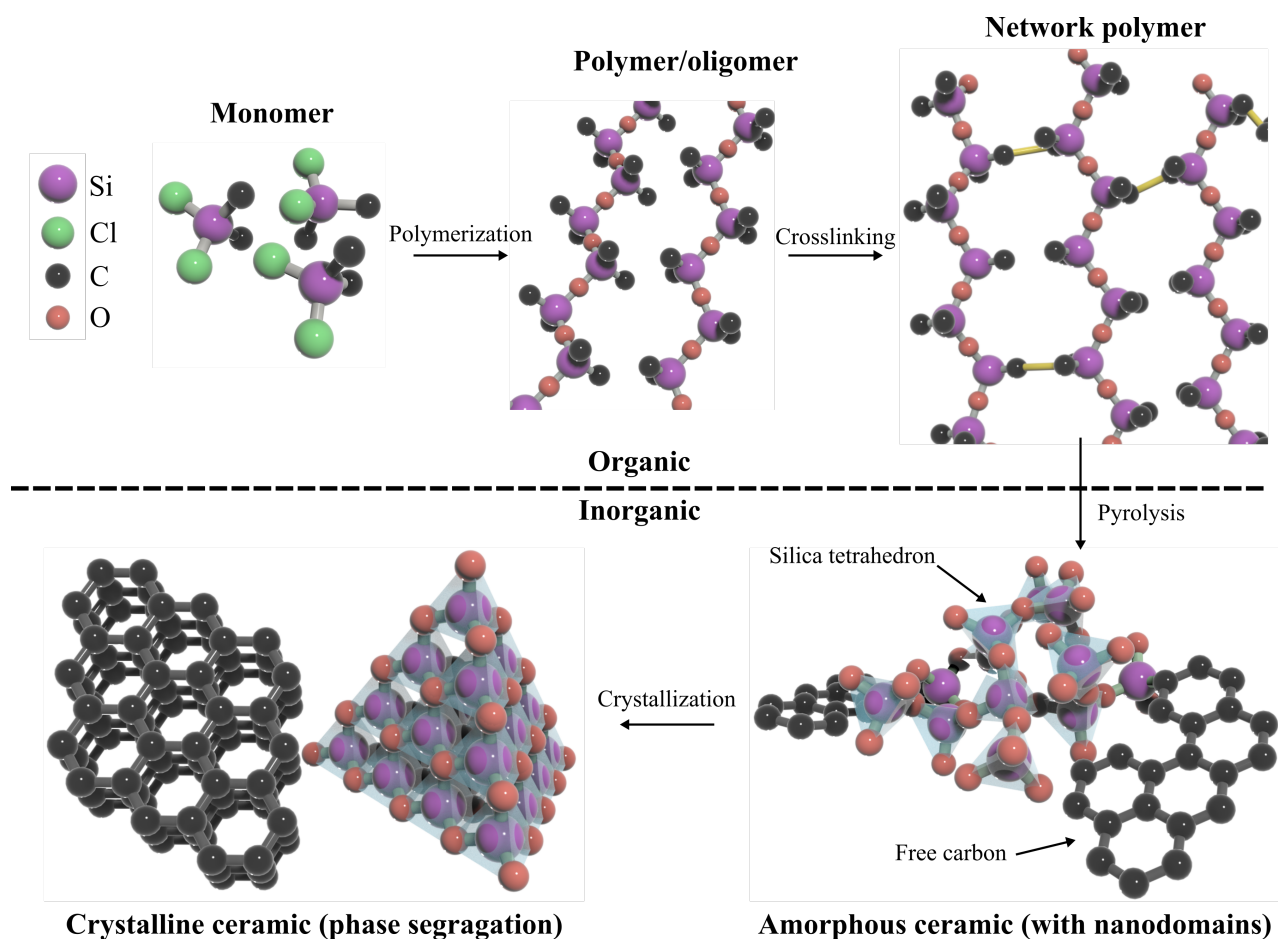


Figure 1.5: *Synthesis of ceramics via the PDC route. Silicon-based compounds are shown as an example.*

in amorphous microstructure during pyrolysis and forming nanodomains of 1-3 nm, which provides good creep and oxidation resistance up to 1500 °C. In addition, some unstable ternary (SiOC, SiCN, BCN) and quaternary (SiOCN, SiBCN, SiBOC, SiAlOC) systems are achievable via PDC route. For example, in a SiOC system, silicon and oxygen remain a silica tetrahedron, but carbon forms free carbon nanodomain structures. PDCs are also unique because the flowability of preceramic polymers allows polymer shaping techniques at relatively lower temperatures while maintaining the macro structures after pyrolysis. For example, amorphous fibers, films, coatings, or composites can only be achieved via PDC synthesis. Because the molecular structures and compositions of preceramic polymers determine the composition, microstructure, the number of phases, and phase distribution of PDCs, chemical reactions can be used to tweak side groups of initial monomers or preceramic polymers

through chemical reactions to control the final properties of ceramics (Figure 1.6¹³).

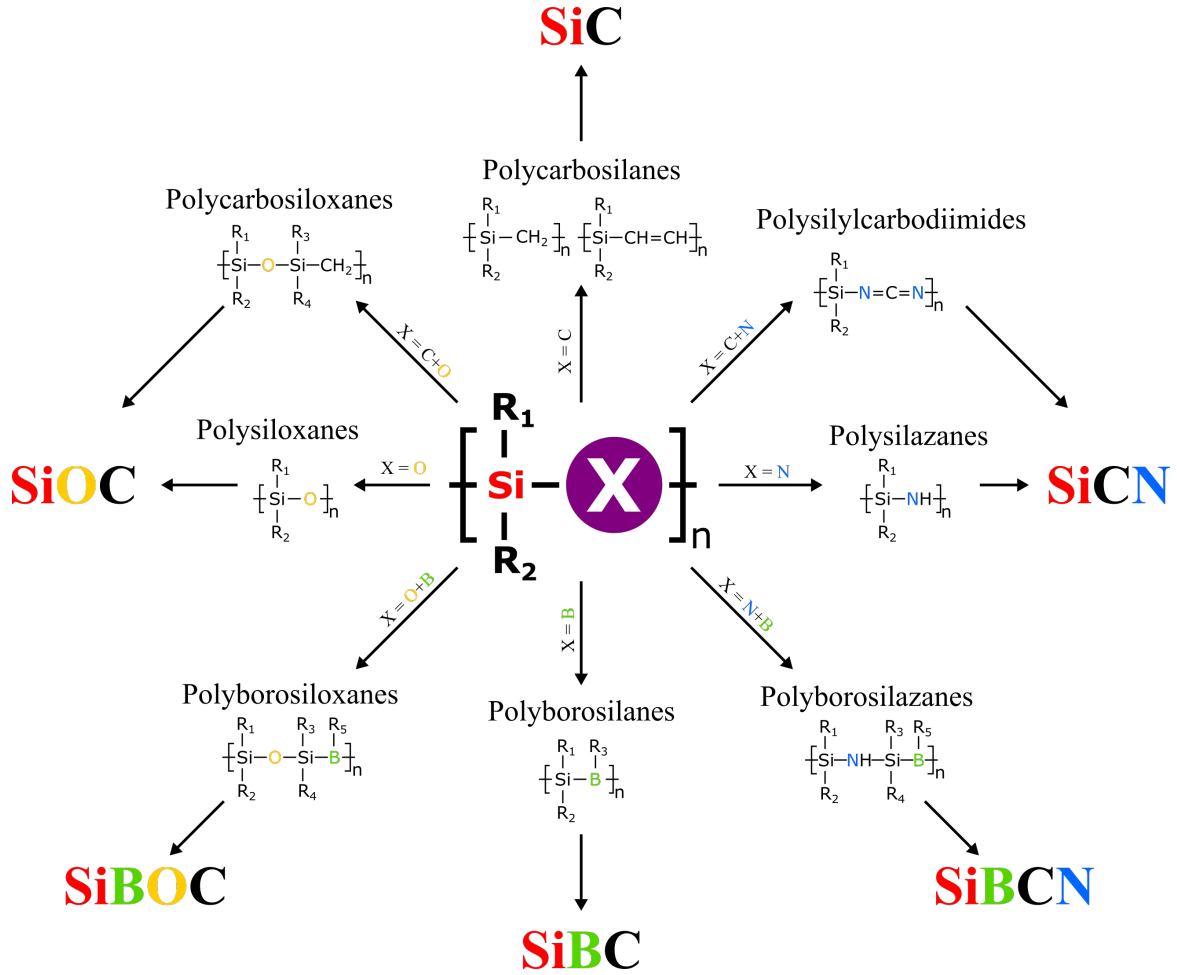


Figure 1.6: Silicon-based preceramic polymers with corresponding PDCs.

1.2.3 PDC Fibers

PDC fibers are one of the most successful PDC products, due to the high demand for developing high-temperature ceramic matrix composite aerospace component, that has been developed over three generations¹³. Serving as the reinforcement, PDC fibers provide strength and structural foundation or shape for the composite, generally in the form of a complex 3D woven structure designed to closely match the final shape of the component²¹. PDC reinforcement in a CMC is added mainly to improve toughness. It is typically in the form of an oxide or nonoxide ceramic fiber that can withstand high application temperatures.

Although oxide-based fibers such as alumina show better oxidation resistance than nonoxide fibers, oxide-based fibers' strength retention and creep resistance at high-temperatures is compromised due to grain growth at elevated temperatures. In some cases, creep rates for oxide fiber can be two orders of magnitude greater than those of nonoxide fibers. Because of lightweight, good oxidation resistance, good thermal shock resistance, and relatively high modulus and strength values, only silicon-based nonoxide ceramic fibers (tending toward SiC composition) are preferred for ultra-high-temperature aerospace applications. Oxide CMCs are perhaps more suitable for relatively less demanding applications^{12;21–23}.

Three different approaches to manufacturing nonoxide ceramic fibers exist—chemical vapor deposition (CVD), extrusion/sintering of powder slurries, and the polymer precursor route. CVD is the oldest method for the production of SiC fibers. In this method, SiC generally is deposited on a heated amorphous carbon or tungsten wire (“core”) resulting in a high-strength fiber^{22;24;25}. Such fibers are monofilaments with a minimum diameter in the range of 75 to 100 microns, which limits their minimum bend radius and renders them unsuitable for weaving into textiles or making complex-shaped ceramic parts. Such high-strength fibers, however, could be used as reinforcement in a metal matrix composite. The extrusion/sintering to make SiC fiber involves spinning SiC powder in a polymeric binder followed by sintering. These fibers are generally thicker than 30 microns, have surface defects, and never fully densify due to difficulty in sintering a nonoxide ceramic^{22;25}. Because high-temperature CMCs would require high-strength flexible ceramic fibers (diameters less than 20 microns), research on alternate routes to obtain continuous and flexible fibers had been ongoing when a discovery in the late 1970s showed how high-temperature ceramic fibers could be made from certain organometallic oligomers or silicon-based polymers using a combination of polymer and ceramic processing methods. This process was later developed into a commercial technology in Japan. These fine fibers show good mechanical properties, thermal properties, and oxidation resistance, and can be woven in textile to make complex-shaped ceramic parts. These SiC fibers are the backbone of the ceramic-fiber ceramic-matrix technology that heralds the next-generation turbine engines. The production of these fibers (Figure 1.7²²) involves steps that are somewhat similar to those used for manufacturing

carbon fibers from polyacrylonitrile (PAN) ^{10;13;22;25;26}: 1. Synthesis of preceramic polymer with desired rheological properties for spinning processes; 2. Melt or dry spinning of the precursor into green fibers; 3. Curing (thermally, chemically, or radiation) of the green fiber to cross-link molecular chains into a duroplastic-like state, rendering it infusible during pyrolysis; and 4. Pyrolysis of green fiber under argon at high-temperature to obtain ceramic fiber.

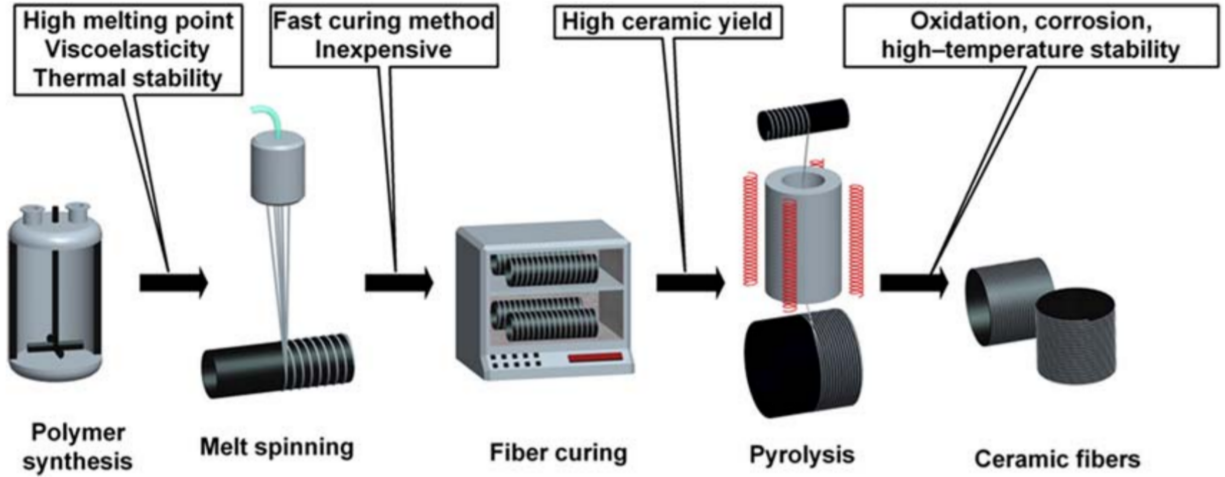


Figure 1.7: *Drawing process of ceramic fibers from PDC route.*

The first generation SiC fibers based on Yajima et al. were spun in inert environments but required curing in the air to make them infusible during pyrolysis at high-temperatures. As a result, such fibers had oxygen in the ceramic upon pyrolysis and the fibers were amorphous, non-stoichiometric Si-O-C instead of crystalline SiC. The relatively poor thermal and mechanical properties of the fiber were attributed to the high oxygen content of these fibers. The second-generation SiC fibers focused on reducing oxygen content by curing the green fibers under gamma or electron irradiation in an inert environment. As a result, these fibers had larger SiC grains along with the graphene-like carbon ²². The third generation fibers were manufactured at even higher pyrolysis temperatures with the addition of trace amounts of aluminum, titanium, or boron to sintering of SiC (the difference between generations are shown in Figure 1.8 ²²). Such fibers are essentially polycrystalline SiC with small amounts of sp^2 carbon phase at grain boundaries. Higher sintering temperature generally leads to larger SiC grain size, elastic modulus, strength, and creep resistance over a wide temper-

ature range. Such fibers, however, are exorbitantly expensive, costing over €18,000/kg²². The high cost of manufacturing SiC fibers is apparently related to the control of oxygen content-costly autoclave techniques are needed for the synthesis of the preceramic polymer while additional pyrolysis steps are required to drive out oxygen from the ceramic fiber. The General Electric Company recently introduced CMC components into its LEAP engines. This innovation is expected to generate tens of billions in new revenue for GE. The development of CMC-turbine blades is rumored. GE Aviation expects that increased jet engine production will increase demand for SiC fibers and tapes as much as tenfold over the next decade. The high cost of these fibers is a major barrier to future growth.

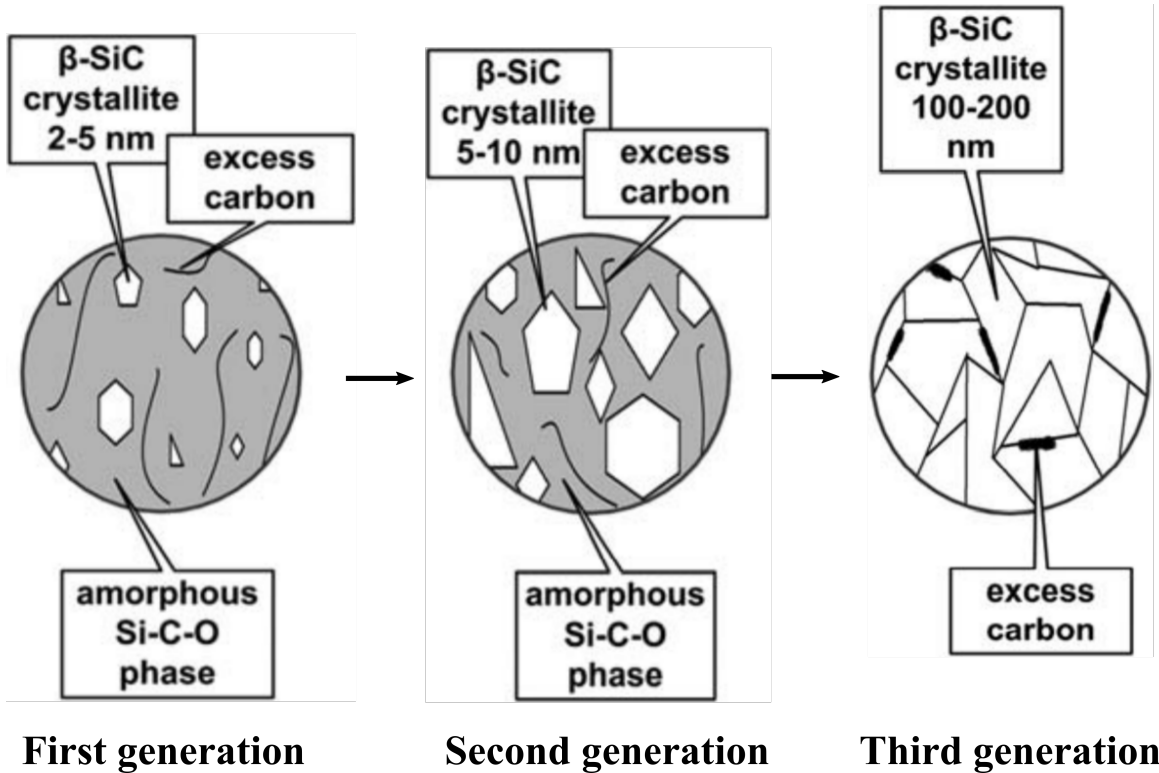


Figure 1.8: *Microstructural difference of SiC fibers between different generations.*

Over the last 25 years, fundamental research in Si-C-O-N compounds yielded new results that show how their nanostructure relates to mechanical properties and thereby provides the insights needed to engineer new compounds for turbine engine applications as follows.

Stability of the amorphous structure: while the binary Si-C crystallizes at 1.200°C, the ternary and quaternary compounds are intrinsically amorphous, with a negative enthalpy of

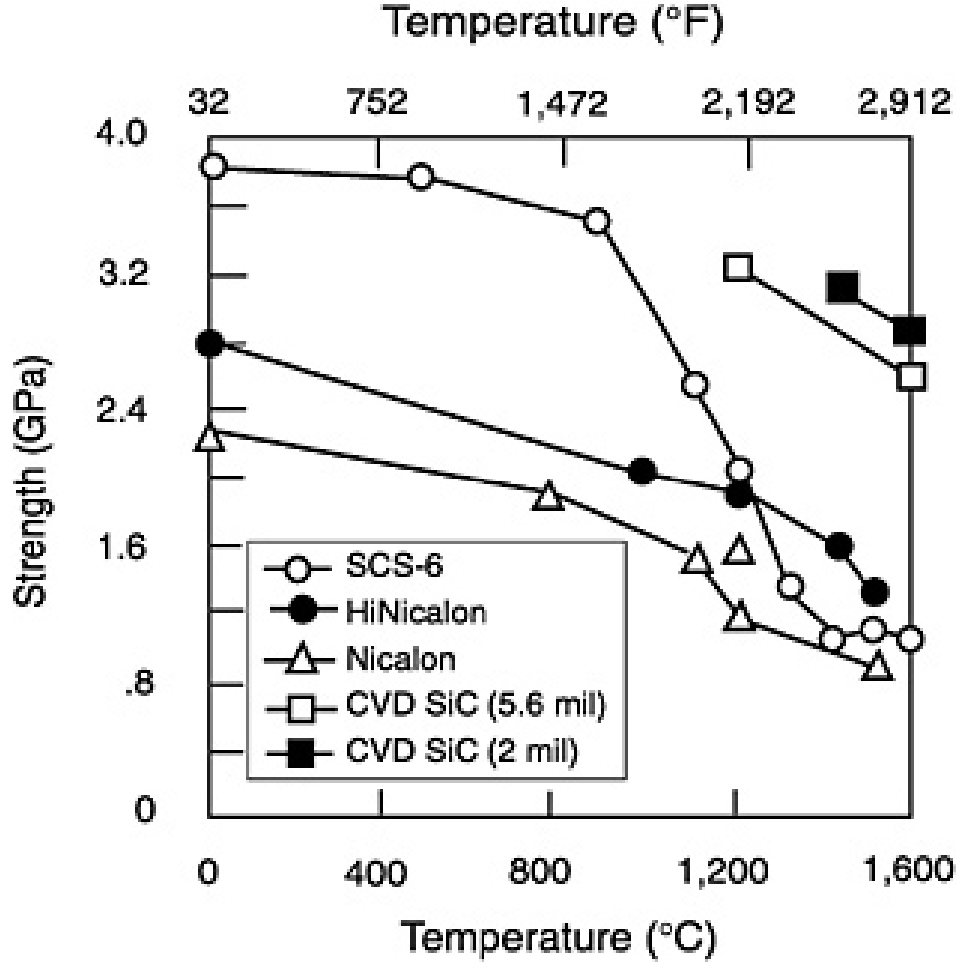


Figure 1.9: *Tensile strength of different ceramic fibers at elevated testing temperature.*

a formation relative to the crystalline state.

The nanodomain network of graphene: the Si-C-O-N materials contain a network of graphene or sp^2 carbon with a domain size of 1-5 nanometers. The domain boundaries consist of mixed bonds of Si-C-(N,O) while the tetrahedral of Si-(O,N) occupies the space within the domains.

Zero creep behavior: the carbon network imparts unusual mechanical properties such as zero creep in the steady-state at temperatures up to 1,500°C, while the interlaced Si-O-N protects the carbon from oxidation.

Polycarbosilane-derived nanocrystalline SiC fibers contain grain boundaries. Although such fibers are known for their ultra-high-temperature stability (Figure 1.9²⁴), the presence of grain boundaries and some low melting phases/impurities at grain boundaries may make

them susceptible to deformation and creep at temperatures as low as 900 °C. For example, the SiC grains may slide relative to one another due to softening at grain boundaries, leading to creep cracks and the eventual deformation of fiber²⁴. In addition, the role of small amounts of oxygen in commercial SiC fibers is poorly understood. In contrast, multi-component amorphous fibers such as SiCN, SiOC, and SiBNC could be produced by a suitable selection of preceramic polymer (Table 1.2). Such ternary and quaternary systems are shown to improve chemical and thermal stability. The SiCNO ceramics are amorphous and contain significant amounts of oxygen, which is rendered harmless by its nanodomain structure of graphene. The synergy between the carbon network and the Si-O-C matrix within which it is embedded imparts thermodynamic stability to the amorphous structure, creep resistance, and, most importantly, the opportunity to manufacture fibers at low cost (polysiloxanes and polysilazanes are significantly more abundant and cheaper than polycarbosilanes-Table 1.2).

Ceramic fibers also generally require an interface compliant coating (100 nanometers to 1 micron thick) and a SiC overcoating to provide a weak fiber/matrix bond in order to realize high toughness in CMCs and to protect the fiber from harsh oxidation environments, respectively²⁷. The coating generally composed of pyrocarbon or hexagonal boron nitride (or a combination of both) has low shear strength and is applied directly to the fibers via CVD techniques^{21;23}. CVD of interface boron nitride and overcoat SiC is expensive, time-consuming, and requires the use of hazardous chemicals; as a result, the costs associated with such coatings could be 10 to 50 times on a square-meter basis than a fabric of carbon or graphitic fiber²⁵.

Future development of PDC fibers can be concluded as follows. 1) New preceramic polymers based on ternary and quaternary systems for CMC matrices: liquid-phase high-purity, low-cost, high-yield polymers that are nontoxic and noncorrosive are being researched at both university and industry levels. Preceramic polymers that can produce amorphous ceramics with Si-XC-N/O, where X is boron, hafnium, or zirconium, the composition is of particular interest due to improved thermal stability and corrosion resistant of the resulting ceramic. Likewise, preceramic polymers that are photocurable (for example, via chemical interfacing with photopolymers) at room temperature are being studied. Polymers that

Table 1.2: *Cost, availability, and properties of bulk PDC ceramics*

Preceramic polymer	Cost	Availability	PDC	Density (g cm^{-3})	Modulus (GPa)	Fracture strength (MPa)	Fracture toughness ($\text{MPa m}^{1/2}$)	Oxidation temperature ($^{\circ}\text{C}$)	Decomposition temperature ($^{\circ}\text{C}$)
Polysilazane	Low-medium	Medium (Commercial)	SiCN	2.3	80-155	<1200	<3.5	~ 1300	~ 1600
Polycarbosilane	High	Limited (Commercial)	SiC	3.1	405	418	4-8	~ 1200	
Polysiloxane	Low	Large (Commercial)	SiOC	2.3	<113	<900	<1.8		
Polyborosilazane	Very high	Very limited (Laboratory)	SiBCN	2.3				~ 1600	~ 2300

contain simpler side (hydrocarbon) groups with a high ceramic yield at increased heating rates are desired in order to minimize the release of volatile components during pyrolysis stages and lower processing costs, respectively larger hydrocarbons, which diffuse out during pyrolysis, could lead to increased porosity in the matrix. This task is not trivial considering that thermal stability and rheological properties of a preceramic polymer are tied to the composition and molecular weight of the side groups.

2) New reinforcement fiber materials: As stated earlier, oxygen-containing amorphous PDC fibers based on ternary and quaternary systems composed of combinations of elements that form strong covalent bonds (such as silicon, carbon, nitrogen, boron, oxygen) and show resistance to crystallization and high-temperature creep should be the focus of future research. Such ceramics could be prepared from preceramic polymers based on polysiloxanes and polysilzanes, which are relatively cheaper and easy to mass-produce compared with carbosilanes. As for fiber processing, preceramic polymers that can be melt-spun or electro-spun are preferred over traditional dry spinning techniques, to keep costs lower due to the reduced number of processing steps. Likewise, polymers that allow rapid inline curing (cross-linking) and pyrolysis with high ceramic yields (greater than 85 percent) are expected to be significantly cheaper and hold low porosity and surface defects.

3) CMC failure prediction: Experimental approaches to understanding ultra-high-temperature thermo-chemo-mechanical behavior of a CMC material could be cost prohibiting. To ensure rapid commercialization of CMCs would require guidance regarding material development and design of fiber preform²⁸. This could be achieved to some extent by developing and employing analytical fiber and CMC material models for time-temperature deformation and rupture behavior. These models may involve computing responses under conditions that induce severe thermomechanical gradients and be able to capture progressive failure of CMCs-CMC material models that accommodate effects of high strain rate and fatigue would be needed for the design of high-speed rotating components inside turbine engines²⁹.

4) Additive manufacturing of PDC CMCs: like PMCs, a variety of additive manufacturing or 3D printing technologies could potentially be employed to manufacture CMCs from silicon-based preceramic polymers. Opportunities exist in the use of preceramic polymers to produce ceramic components in a range of compositions using either

conventional stereolithography printing (via chemical interfacing with photopolymers) or direct extrusion-based fused deposition modeling of composite slurries followed by pyrolysis at high-temperatures³⁰. The challenge lies in the ability to produce uniform, large-area, defect-free components with desired thermomechanical properties in an economical manner. Very limited data have been reported in the literature on such composites-some new reports from the Air Force Research Laboratory, HR Lab, and university researchers in Italy and the United States have started to emerge³⁰.

1.2.4 Additive manufacturing of PDCs

The extremely high processing temperature of conventional ceramics causes a great challenge for producing complex-shaped ceramics, and the brittle nature of ceramics limits opportunities for casting or machining as well. Additive manufacturing, however, provides a solution for generating those complex structures³¹. Although early established ceramic additive manufacturing (AM) or 3D printing techniques were focused on how to bond ceramic powders into 3D structures, the ceramic powders still had to be locally sintered to the high melting temperature via selective laser sintering (SLS) or cured with binders that had to be removed with additional thermal treatment. Intrinsic porosity and residual stress caused by sintering resulted in low mechanical strength of the printed parts.

PDC route with additive manufacturing is a promising alternative to the conventional powder route because preceramic polymers can be processed simply by techniques applicable to polymers. The most significant advantage of the polymer-derived molecular method is the tweakable properties of preceramic precursors: photosensitive (UV active) preceramic polymers can be synthesized via modified organosilicons with essential functioning groups (thiol, vinyl, acrylate, methacrylate, or epoxide) connected to the silicon backbone. This alteration will greatly lower the processing temperature when applied to stereolithography (SLA) systems (Figure 1.10^{31;32}). However, shrinkage and porous structures may form during polymer-to-ceramic conversion, making PDC-associated additive manufacturing techniques more suitable for generating very small (micro to submicron), porous and complex structures

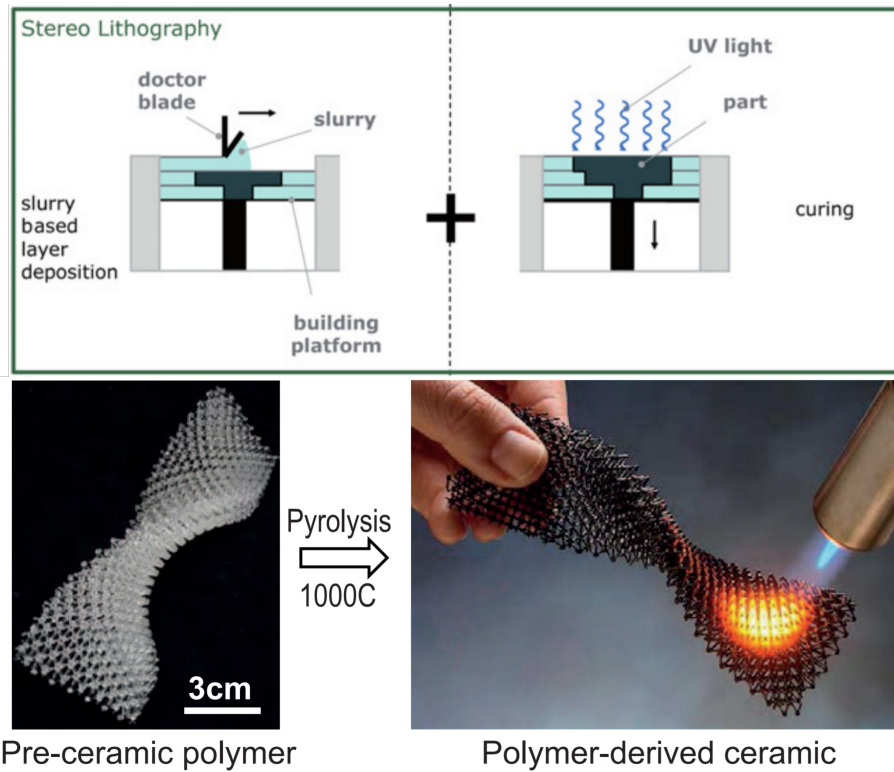


Figure 1.10: *Stereolithography of ceramics (Top). Image of printed ceramic part (bottom left) and pyrolyzed part (bottom right).*

rather than dense bulk products.

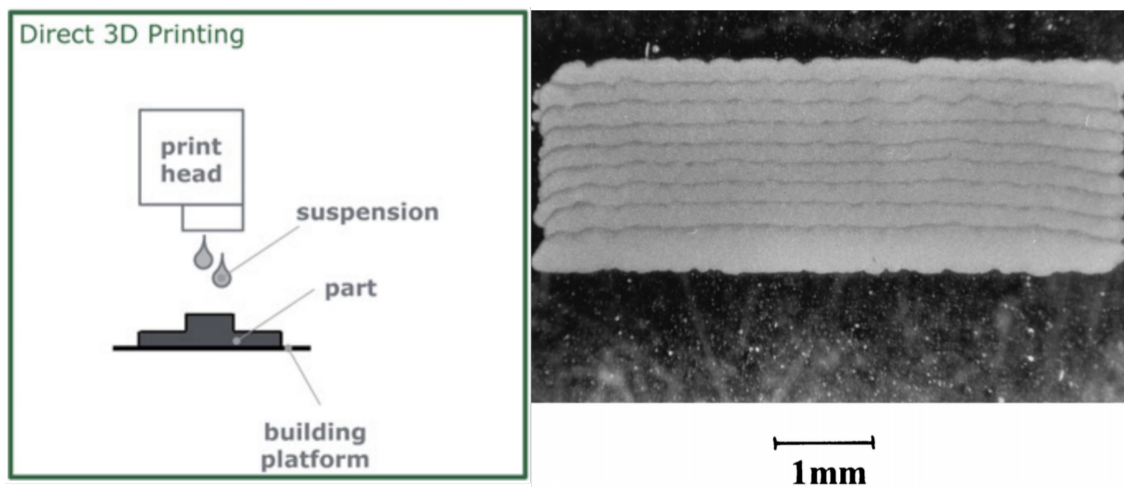


Figure 1.11: *Ink jet printing of ceramics (left). Image of printed ceramic part (right).*

One of the earliest applications of PDC 3D additive manufacturing was performed on a multilayer inkjet printer³³ (as shown in Figure 1.11^{32;33}). Mott et al. used polycarbosilane

(PCS) as the resin and the binder for pre-existing SiC powder with a solvent suspension system. Nozzle size, viscosity, and ink drying speed were used to achieve $\sim 100\mu\text{m}$ diameter and $3\mu\text{m}$ thickness of the droplets. Although PCS effectively controlled distortion, defects, and cracks, droplet spreading significantly affected the precision of the printed parts.

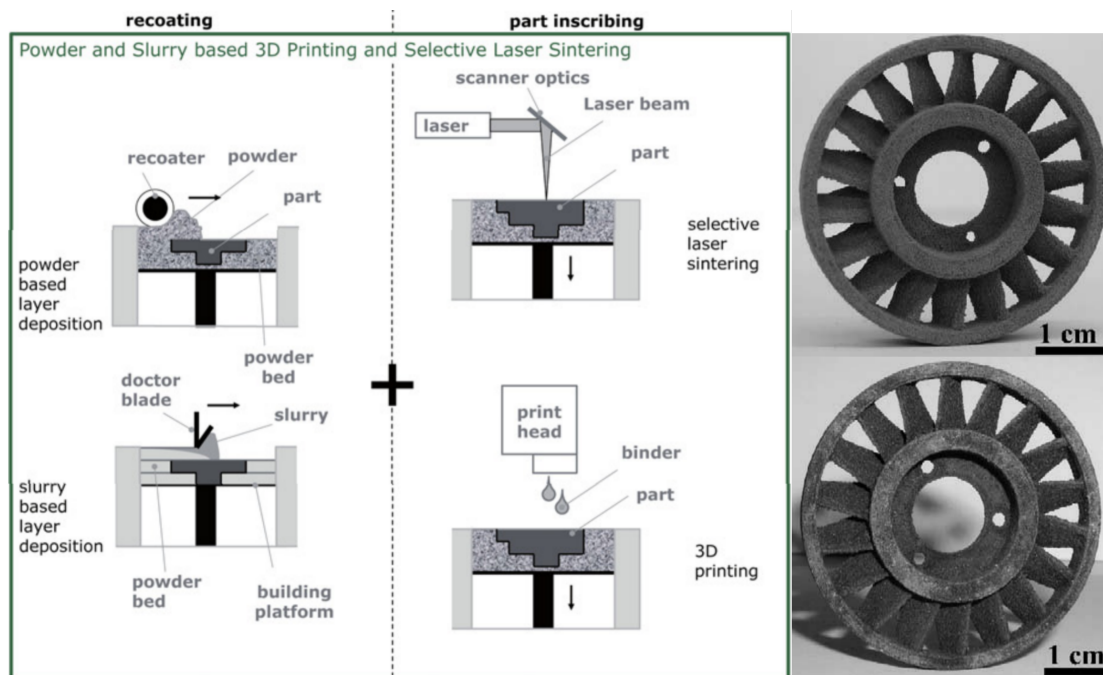


Figure 1.12: *Selective laser sintering of ceramics (left). Image of printed part (right top) and pyrolyzed part (right bottom).*

As an alternative to SLS (Figure 1.12^{32;34}), which is primarily applied to ceramic powders, a modified technique known as selective laser curing (SLC) has been reported for PDC-based ceramic components³⁴. Similarly, SLC locally irradiates a laser on a uniformly spread, very fine powder bed to harden the targeted area; however, SLC only needs to raise the processing temperature to approximately $400\text{ }^{\circ}\text{C}$ to melt and cure preceramic polymers. Because no binders or binder removal steps are utilized in a PDC SLC system, shrinkage during polymer-to-ceramic conversion is greatly reduced and the generation of near-net-shape is not restricted by significant shrinkage. While SLS locally heats ceramic particles to extremely high melting temperatures so the thermal gradient may result in residual thermal stress and cause distortion of the printed part. decreased processing temperatures in an SLC system improves precision by reducing thermal stress from partial heating.

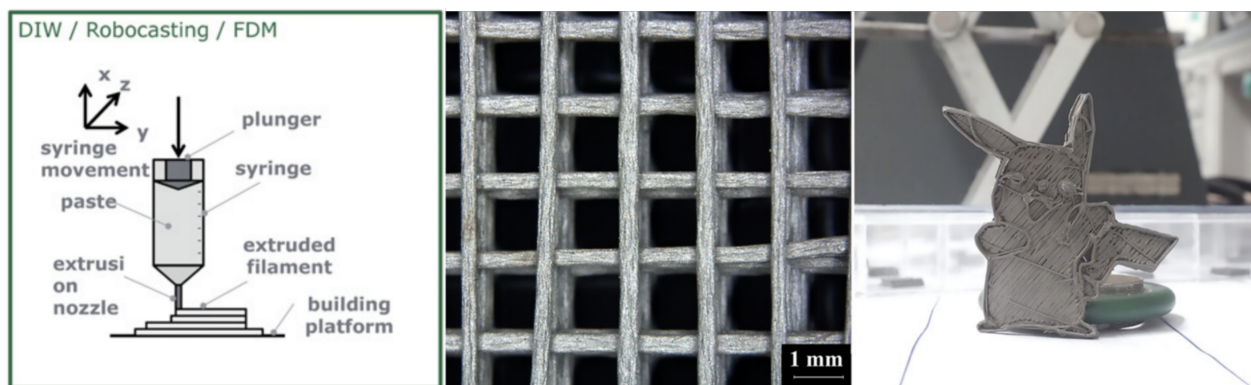


Figure 1.13: *Direct writing of ceramics (left). Image of printed part (center) and pyrolyzed part (right).*

The direct ink writing (DIW) technique has recently been incorporated into 3D printing of PDC and PDC based CMCs^{35;36} (Figure 1.13^{32;36}). The DIW technique and fused deposition modeling (FDM) both extrude the filament materials, such that the precision of the extrusion is controlled by the nozzle size, but, DIW applies shear-thinning ink with sufficient strength to support extruded structures³⁷. The ink contains preceramic polymer powders and solvent with a crosslinking agent. In addition, extra crosslinked polymer powders may be required to adjust the viscosity and flowability of the printing paste. Because the extruded materials do not experience in-situ crosslinking or hardening, however, low-temperature heat treatment (for crosslinking) is essential to crosslink dissolved preceramic polymers. The extrusion nature of DIW suggests that scaffold structures are typically generated by this technique; therefore, the strength or rheology of the ink determines the structure and upper limit of the size of printed parts. and the ink composition is tweakable with enhancement, such as graphene oxide or carbon nanotubes. Since the addition of enhancement alters the viscosity and flowability drastically, if the enhancement concentration is controlled to provide sufficient printing strength, direct writing of CMCs is then achievable.

All additive manufacturing systems reported for the PDC process may finish curing of the preceramic polymers within the system, so the pyrolysis (post-heat-treatment) of printed green bodies must occur at about 1000 °C to allow a full polymer-to-ceramic conversion. Significant shrinkage and porosity during this stage must be considered before component

design; fillers, such as SiC, Cr, and MoSi₂, were applied in some researches to reduce shrinkage.

1.2.5 Ceramic matrix composites

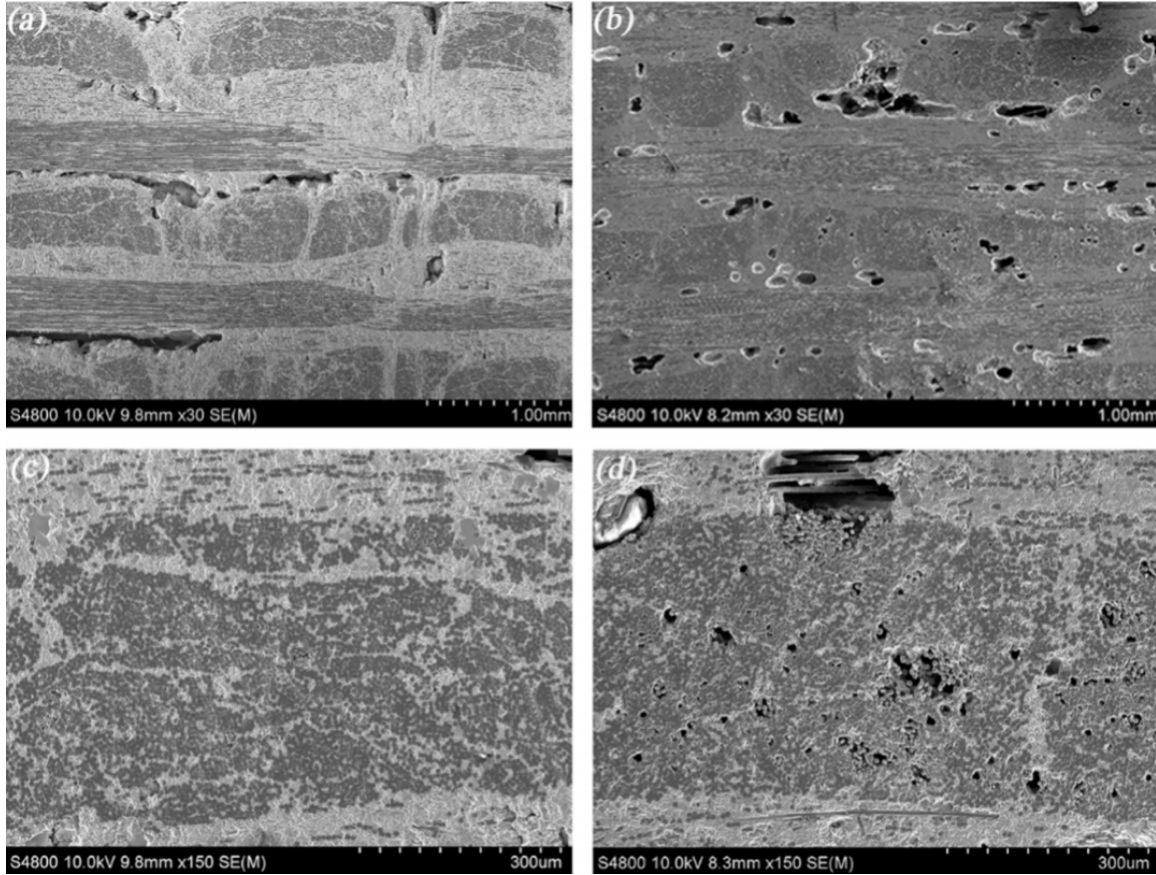


Figure 1.14: SEM images of the cross sections of (a, b) Liquid phase derived-Cf/SiC composites and (b, d) Solid phase derived-Cf/SiC composites.

Table 1.3 shows the varieties of oxide and non-oxide ceramics as a matrix of CMCs with applicable reinforcements⁹. In 1969, Crivelli-Visconti and Cooper introduced carbon fiber (CF) as a reinforcement for an alumina ceramic matrix. This early research resulted in a toughened ceramic composite and showed that weak fiber-matrix bonding produces increased strength and higher fracture toughness. Carbon-based nanomaterials, especially graphene and CNTs have shown to enhance CMC materials due to their high Young's modulus (> 1 TPa). Many research articles have also reported enhanced mechanical properties when

carbon nanomaterials are incorporated into a ceramic matrix (such as Cf/SiC composites shown in Figure 1.14), thereby reinforcing, toughness, crack resistance, thermal conductivity, and contact-damage resistance.

Despite the enhanced mechanical performances, however, the application of carbon-based materials as reinforcement of CMC materials has received far less attention than polymer matrix composites (PMCs) due to the different enhancing mechanisms. One toughening mechanism in CMC is based on a bridging effect of the reinforcement between crack surfaces, where the reinforcements are directly exposed to a harsh corrosive environment and rapidly lose their functionality. This will limit the working temperature to the moderated thermal environment (less than 500 °C) compared to the potential applications of CMCs (more than 1000 °C in the oxidation environment for aerospace purposes).

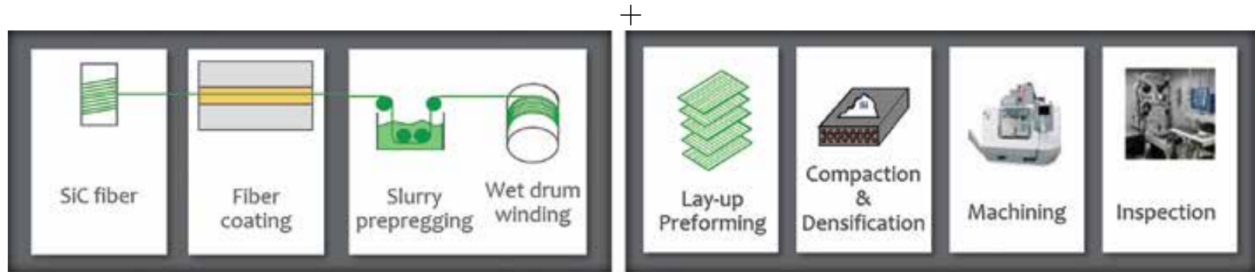


Figure 1.15: *Schematics of SiC/SiC composite production process.*

Later in 1971, Lindley and Godfrey fabricated of SiC ceramic-fiber-reinforced Si_3N_4 material with 60 % enhanced strength and toughness increased by 2-3 orders of magnitude, compared to unreinforced Si_3N_4 . Subsequent research reported CMCs with enhanced properties. Due to the promising high-temperature capabilities of CMCs (e.g., high specific strength with low specific weight, thermal resistance over a wide temperature range, and enhanced tolerance from monolithic ceramics), CMC materials are advantageous for high-temperature structural applications such as bearing structures, brake components, or aerospace applications.

The current status of CMC research has reached spatial scale design of the structure where 3D woven continuous fiber bundles are oriented into patterns (known as preforms or preregs as shown in Figure 1.15). The woven structure in certain orientations can guide the

Table 1.3: *Varieties of CMC matrices and reinforcements.*

	Matrix	Particulates	Platelets	Whiskers	Fibers
Oxide	Al ₂ O ₃	ZrO ₂ , SiC, TiC, TiN, TiB ₂ , ZrB ₂ , metals	SiC	SiC, B ₄ C	SiC, Al ₂ O ₃ , 3 Al ₂ O ₃ · 2 SiO ₂
	Y–ZrO ₂ ¹	Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	
	ZrO ₂ ²	Al ₂ O ₃	SiC		
	3 Al ₂ O ₃ · 2 SiO ₂	Al ₂ O ₃ , ZrO ₂			
	Y ₃ Al ₅ O ₁₂			Al ₂ O ₃	Al ₂ O ₃
	MgO · Al ₂ O ₃	Al ₂ O ₃			
	Na–β–Al ₂ O ₃	ZrO ₂			
Non-oxide	SiC		SiC	B ₄ C	C, SiC
	Si ₃ N ₄	SiC, TiC, TiN, TiB ₂	Si ₃ N ₄	Si ₃ N ₄	SiC, Al ₂ O ₃ , C
	MoSi ₂	ZrO ₂ , TiB ₂ , Nb, SiC, Si ₃ N ₄	Al ₂ O ₃	SiC	SiC, Al ₂ O ₃
	B ₄ C	TiB ₂ , Al ₂ O ₃	SiC	SiC	C, SiC
	BN ³	B ₄ C			
	AlN			SiC	
	TiB ₂	B ₄ C, BN			

¹Tetragonal²Partly stabilized³Hexagonal

major load paths and magnify the interlocking of fiber bundles, thereby enhancing strength and preventing sudden failure or delamination of the entire structure. The large interspace between fiber bundles may be filled partially with rods that orient without a preferential direction to control local cracking.

CMC manufacturing

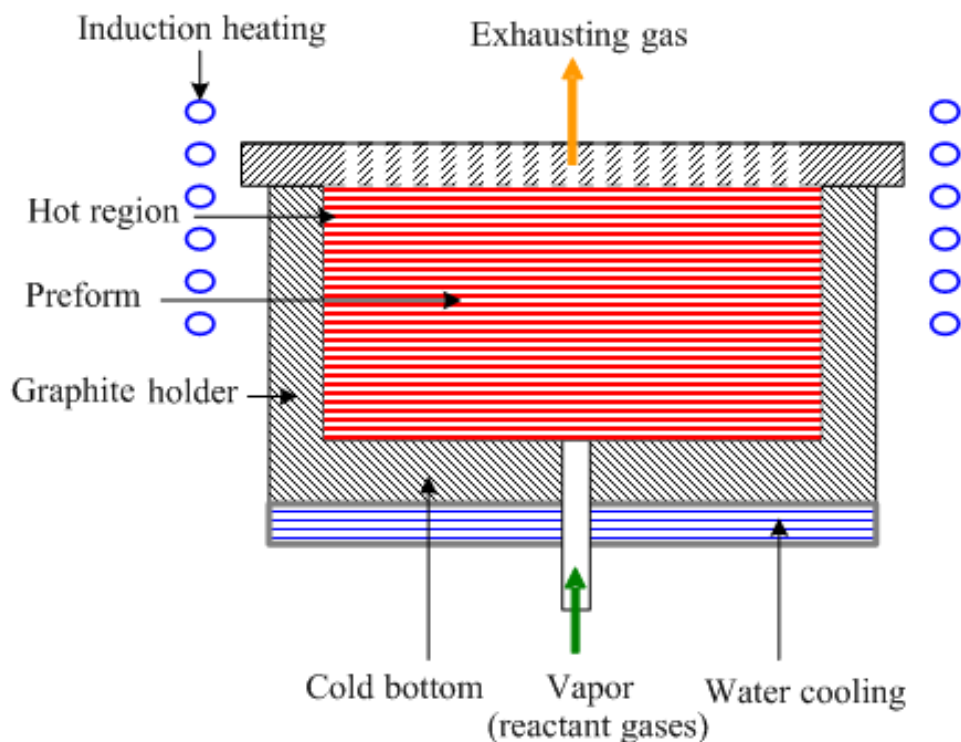


Figure 1.16: *Schematics of CVI process.*

CMCs are mainly processed via four different techniques. All CMC fabrication techniques discussed in this section are matrix processes on arranged fiber preforms. Depending on the phase of the matrix precursor, the techniques are chemical vapor infiltration (CVI, gas-phase route), polymer impregnation and pyrolysis (PIP, liquid phase routes), reactive melt infiltration (RMI, molten phase route), or slurry infiltration and hot processing (SI-HP, slurry phase route). During fabrication, factors such as matrix uniformity in preforms, residual porosity of the matrix, fiber-matrix bonding, and fiber degradation control the final properties of the CMC products.

In the CVI technique, vapor-phase precursors carry out all infiltration and deposition of the matrix, including interphase fiber coating and sealing coating. The infiltration process typically is performed in steady-state isothermal and isobaric conditions (known as I-CVI). The rate of densification is then enhanced with temperature gradient (TG-CVI) or pressure

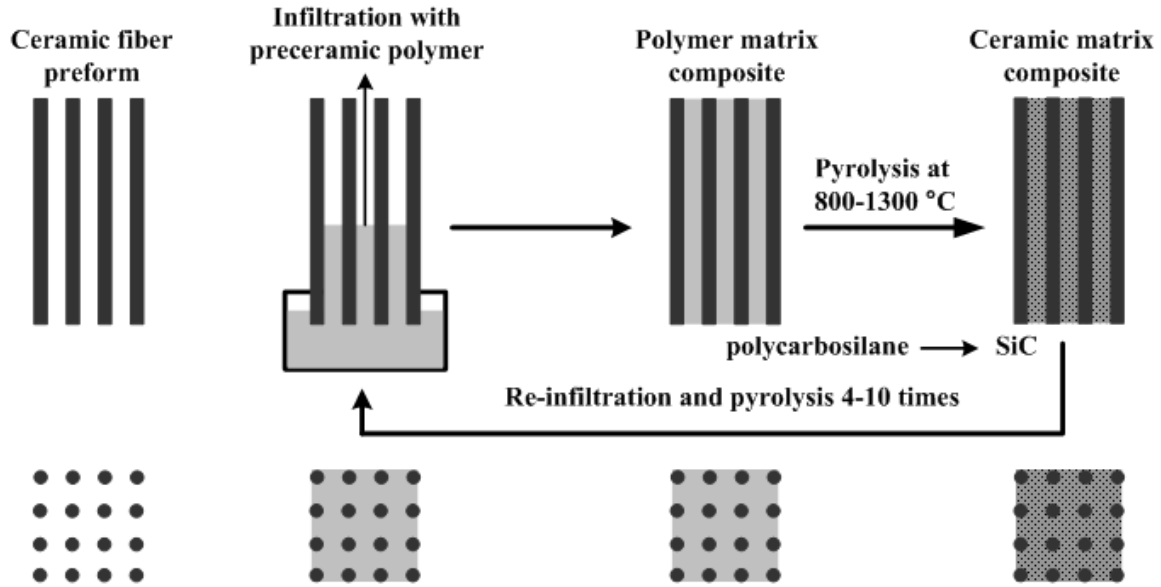


Figure 1.17: Schematics of PIP process.

gradiance (P-CVI). The number and size of preforms are limited only by the size of the furnace, meaning this technique is advantageous for industrial applications.

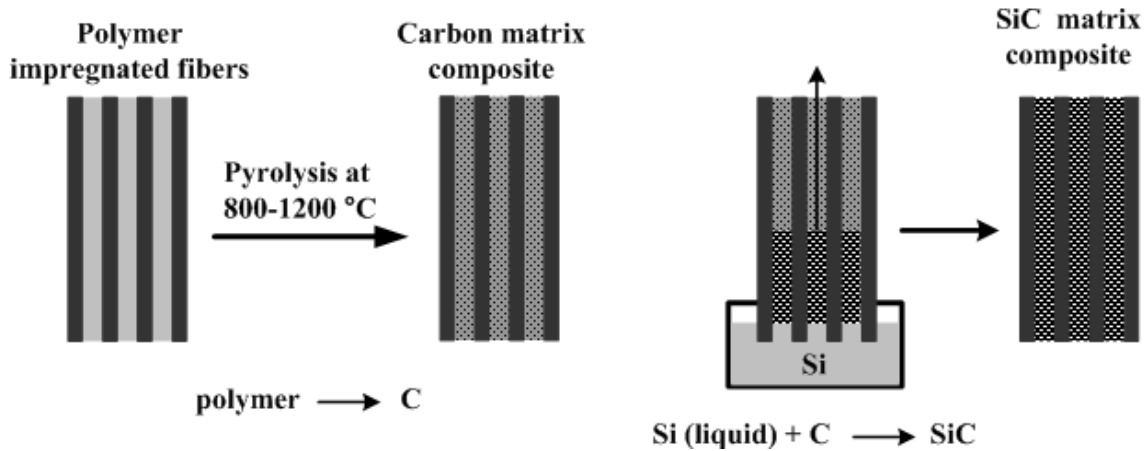


Figure 1.18: Schematics of RMI process.

Prior to liquid-phase PIP, a powder-based PDC technique is applied in which the preform structure filled with polymer powders is crosslinked and pyrolyzed in an inert environment at a temperature greater than 1000 °C. However, reimpregnation is necessary to obtain a denser PIP fabricated structure. This cycling process (reimpregnation) is reduced by 50 % if a liquid-phase polymer precursor is used.

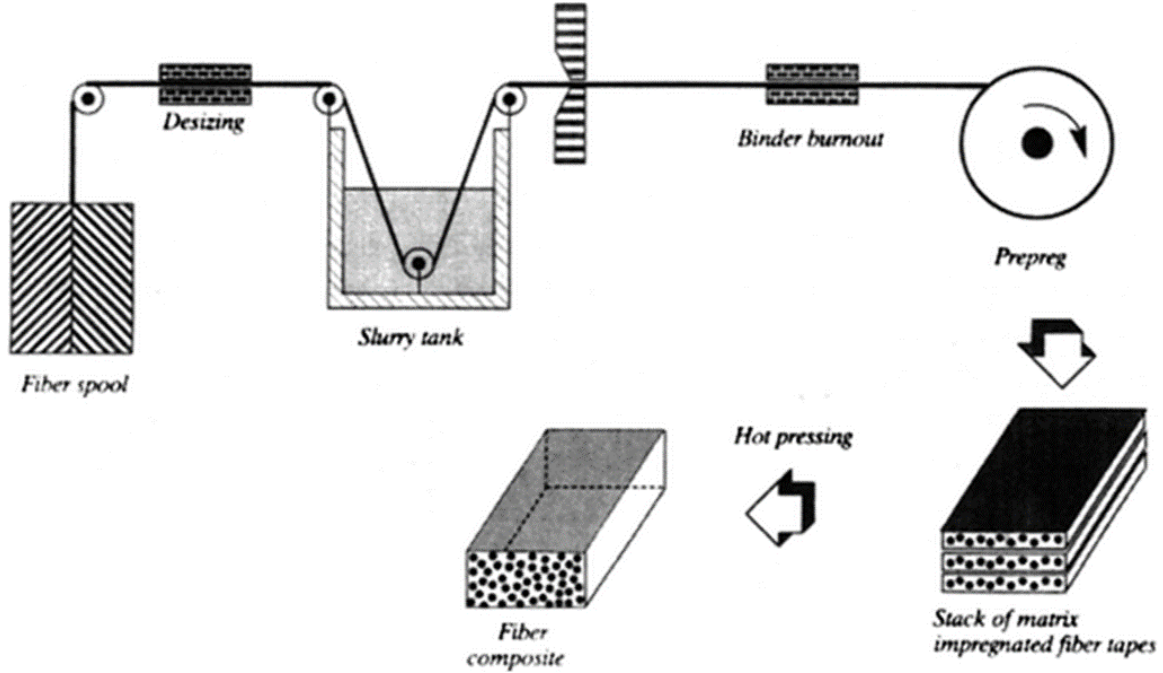


Figure 1.19: *Schematics of SI-HP process.*

The RMI technique requires carbon to be pre-deposited on the preform fiber surfaces, so molten silicon will react (exothermal) with the carbon at a high-temperature and form a SiC matrix with a free silicon phase. However, the excessive silicon phase damages the creep resistance and thermal stability. Comparatively, SI-HP elevates temperature high enough to directly sinter SiC particles, potentially resulting in degradation of the preform fibers.

Table 1.4 summarizes the advantages and disadvantages of the described processing techniques. As shown in the table, although low fabrication temperature is easily achievable, it slows down the densification process and results in high residual porosity. On the other hand, increased process temperature increases handling difficulty and exposes fibers to a higher risk of degradation. Hybridization of two techniques (e.g. CVI/RMI and PIP/RMI) may resolve mutual disadvantages.

CMC toughening mechanism

Implementation of fiber-reinforced polymer matrix composites (FRPMCs) as structural materials has led to increased attention on composite materials for high working temperatures.

Table 1.4: *Comparison of CMC fabrication techniques.*

Technique	Processing temperature (°C)	Processing pressure (MPa)	Advantages	Disadvantages	Matrices
CVI	900-1100	<0.1	Low fiber degradation; High microstructural quality.	Low densifying rate; High residual porosity of 10-15 %.	Carbide, nitride carbon, oxides, borides
PIP	800-1100	2	Low process temperature and pressure.	Repeating needed for densification; High porosity in the matrix.	Silicon carbide, silicon nitride, silicon carbide nitride
RMI	1400-1600		Fast densification; Low residual porosity of <5 %; Hybrid capability.	Fibers need high thermal stability; Matrix contains a free Si phase.	SiC
SI-HP	1700-1800	~25	Fast densification; Near dense structure; High thermal stability.	Fibers need high thermal stability; Limited scalability.	Oxides

Knowledge from PMC may benefit the early development of FRCMCs for structural applications, but, the production, microstructure, and mechanical properties differ significantly between the two composite systems (as shown in Figure 1.20). Fibers in PMC systems are much stronger than matrices in modulus and strength, meaning the reinforcement provides the stiffness and loadbearing. A strong fiber-matrix interfacial bond is preferred to maximize the load distribution effect of the matrix. In addition, although low strain capability causes fiber failure prior to the matrix, the strength and modulus of the reinforcement are only slightly greater than the already strong ceramic matrix.

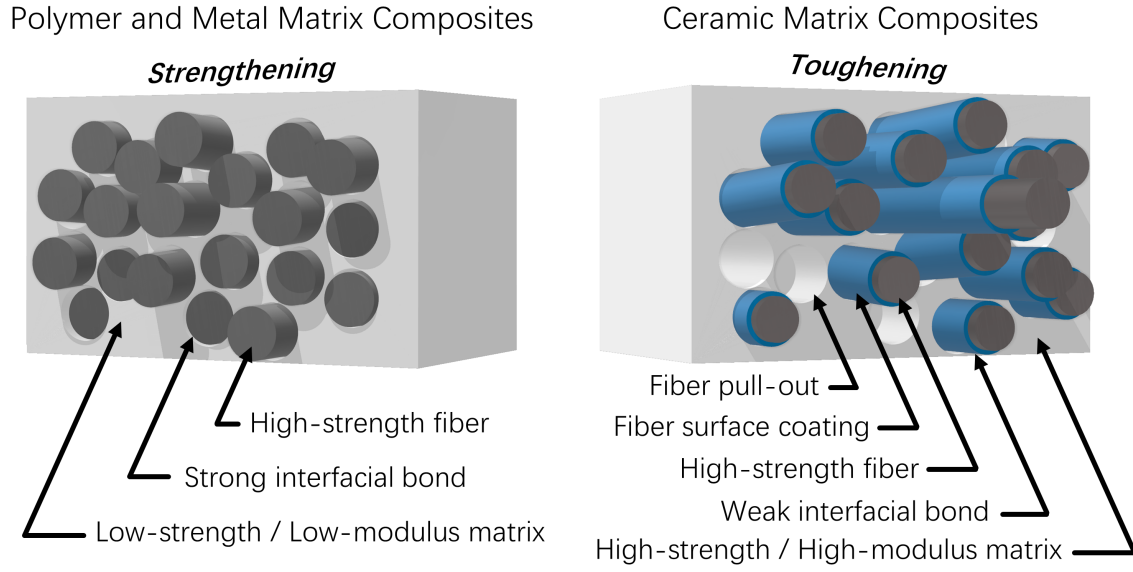


Figure 1.20: *Different enhancing mechanisms and purposes in PMC and CMC.*

Table 1.5: *Comparison between PMC and CMC.*

Different factor	PMC	CMC
Fiber/matrix engineering properties relation	$\sigma_f \sim 100\sigma_m$	$\sigma_f \sim \sigma_m$
	$E_f \gg E_m$	$E_f > E_m$
	$\epsilon_f < \epsilon_m$	$\epsilon_f \geq \epsilon_m$
Fiber-matrix interface	Strong interface	Weak interface
Reinforcing purpose	Strength, stiffness	Toughness
Fracture control	Fiber controlled	The first matrix, then fiber-enhanced

Fibers increase system toughness but crack propagation through the fibers due to strong interfacial bonding negatively impacts fracture toughness. Compared to the polymer matrix, the ceramic matrix usually exhibits high pores, processing defects, microcracks, and residual thermal stress. The differences between PMC and CMC are summarized in Table 1.5.

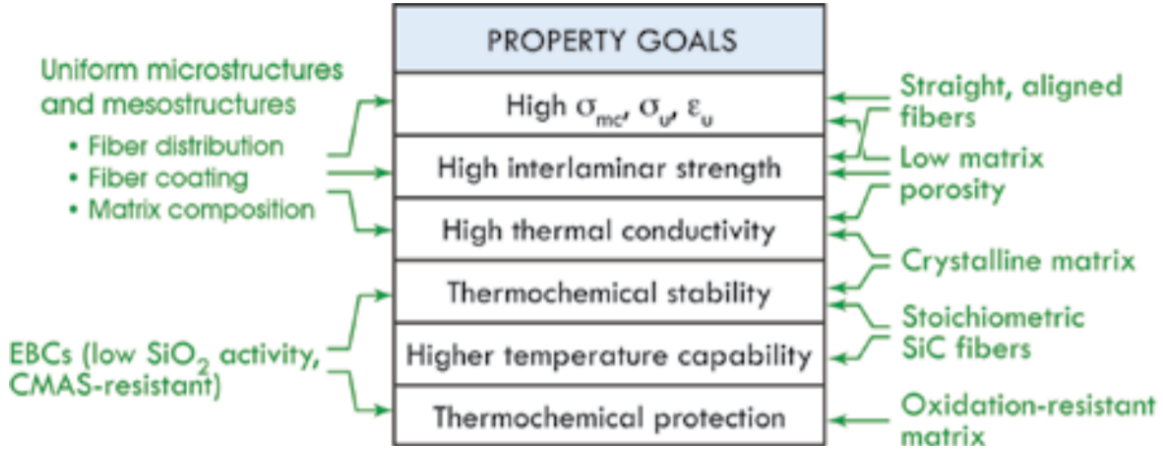


Figure 1.21: *Property goals to be achieved by structural implementation.*

As discussed, fracture toughness of CMCs is an essential factor for determining the mechanical reliability of a component. Other property goals, with corresponding implementation factors, are shown in Figure 1.20. Ceramic toughness determines application boundaries and CMC innovation.

According to R. W. Rice, fracture toughness, a key design factor of ceramic materials, quantitatively measures how readily a material resist crack propagation and fracture. According to Griffith's theory of fracture, there are three fracture modes, crack propagation most often occurs in opening mode (Mode I) for highly brittle materials, while sliding mode (Mode II) and tearing mode (Mode III) usually apply to glide motions of dislocations (edge and screw). For a crack with a length of $2a$, the corresponding relationship of fracture strength (σ_f) is:

$$\sigma_f = \sqrt{\frac{2E\gamma}{a}} \quad (1.1)$$

where, E is Young's modulus of the material, and γ is the crack surface energy. This equation can be rearranged with stress intensity factor K at the crack tip (r, θ):

Table 1.6: *Fracture toughness of CMCs at room-temperature and high-temperature.*

Composite	K_{IC} at RT (MPa m ^{1/2})	K_{IC} at HT (MPa m ^{1/2} at °C)	σ_f at RT (MPa)	σ_f at HT (MPa at °C)
CVI-SiC/SiC	30	30 at 1400	300	280 at 1400
PIP-C/SiC	27.2		450	
CVI-SiC/Si ₃ N ₄	13		965	
SiC/MoSi ₂ -Si ₃ N ₄	35	65 at 1400		
Si ₃ N ₄ /BAS ¹	6.8		921	
SiC/Al ₂ O ₃	28	16 at 1400	461	340 at 1400
Al ₂ O ₃ /Al ₂ O ₃	17	9 at 1000	404	162 at 1000
YSZ ² /Al ₂ O ₃	2.6	2.6 at 1000	354	287 at 1000

¹BAS: barium aluminosilicate, BaO · Al₂O₃ · 2 SiO₂

²YSZ: yttria stabilized zirconia, Y–ZrO₂

$$\sigma = \frac{K}{\sqrt{2\pi r}} f(\theta) \quad (1.2)$$

where f is a function of θ . When K reaches critical value K_{Ic} (critical value for Mode I, or fracture toughness), fracture occurs rapidly. ASTM standard testing methods measure and calculate fracture toughness, as detailed in document C1421-99. Fracture toughness, the fracture strength of the most widely used CMCs are shown in Table 1.6.

Toughening mechanisms for particulate reinforced and fiber-reinforced ceramic composites differ slightly; FRCMC toughening mechanisms are discussed in detail in the following sections. Chawla analyzed the stress-strain curves of typical CMCs to illustrate the fracture process with the following detectable features:

1. The specimen shows an elastic property up to a proportional limit.
2. Microcracks generate in the matrix.
3. The cracks propagate around fibers and form fiber bridging at the crack surface.
4. Fiber debonding and pull-out occur, followed by complete failure.

These four characteristics correspond to the four important toughening mechanisms in the FRCMCs.

Microcracking

Microcracking toughening occurs at the early fracture stage that is existing as well in monolithic ceramics. Microcracks, which are formed near a high-stress zone around the macroscopic crack tip, provide crack shielding effects by reducing the elastic modulus of the material and microcrack propagation. According to Giannakopoulos et al. the applied stress intensity factor K^∞ has the following relation with near tip stress intensity factor K :

$$\frac{K^\infty}{K} = \left[1 + \frac{1.094}{1 - \nu_m^2} \left(\frac{E_m}{E_s} - 1 \right) \right]^{1/2} \quad (1.3)$$

where, ν_m is the Poisson's ratio of the matrix. The ratio of $E_m/E_s = [1 - 16d_s/9]^{-1}$ is determined by the saturated microcrack density d_s that is related to the matrix grain size.

Crack deflection

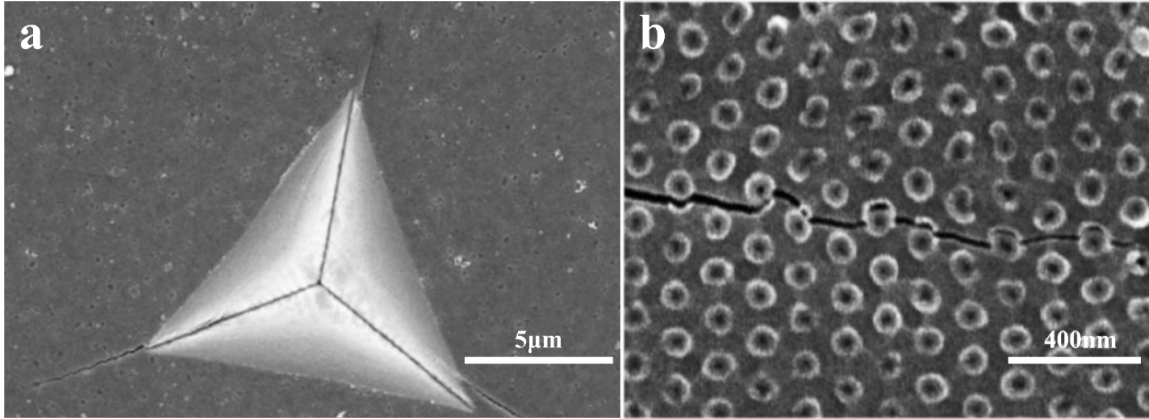


Figure 1.22: SEM images of (a) top indentation with induced crack and (b) crack deflection and propagation along the fiber-matrix interface in CNT reinforced Al_2O_3 composite.

Crack deflection toughening theoretically occurs in any second-phase (including both particulates or fiber) reinforced composites when the crack tip interacts with the fiber-matrix interface. In FRCMCs the crack typically grows transversely in the fiber longitudinal direction. The mechanism is simply concluded that the crack tip reaches the interface of the reinforcement where the interface is weakened, and the crack deflects further in an out-of-plane direction rather than propagate through the reinforcement and cause brittle fracture

of the structure. The result is observed as decreased stress intensity factor (K) at the crack tip, or equivalently, raises the energy for further crack growth. Faber, et al., proposed the following crack deflection toughening model:

$$\frac{K_c}{K_0} = \left(\frac{E_c}{E_0} (1 + 0.87f) \right)^{1/2} \quad (1.4)$$

where, K_c and K_0 are reinforced and unmodified toughness, respectively, of the matrix, E_c and E_0 correspond to the reinforced and unmodified modulus, respectively, of the matrix, and f is the volume fraction of reinforcement. Hu et al. proposed the following fiber-matrix interface fracture criterion (energy release rate criterion):

$$\frac{G_d}{G_p} < \frac{\Gamma_i}{\Gamma_f} \quad (1.5)$$

where, G_d and G_p represent deflection and propagation energy release rate, respectively, and Γ_i and Γ_f are surface energy of fiber or fiber-matrix interface, respectively. According to Bengisu et al., crack deflection is easily initiated at two conditions: weak second phase/matrix interaction, and residual strain generated by the mismatching of elastic modulus or thermal expansion between reinforcement and matrix. The energy release rate and toughness have the following relationship:

$$K_{Ic}^2 = E^* G_{Ic} \quad (1.6)$$

where, $E^* = E / (1 - \nu^2)$ for plane stress and ν is Poisson's ratio.

Crack bridging

Crack bridging toughening is enabled reinforcement-enhanced composites such as particulates, rods/whiskers, or long fibers. When the crack front is driven to and passed through the reinforcement, the bridging of reinforcements between the crack surfaces forms. For particle-reinforced or fiber-reinforced matrices, particles are strongly bonded to the matrix and consume the energy of plastic deformation. In contrast, the bridging of the fibers oc-

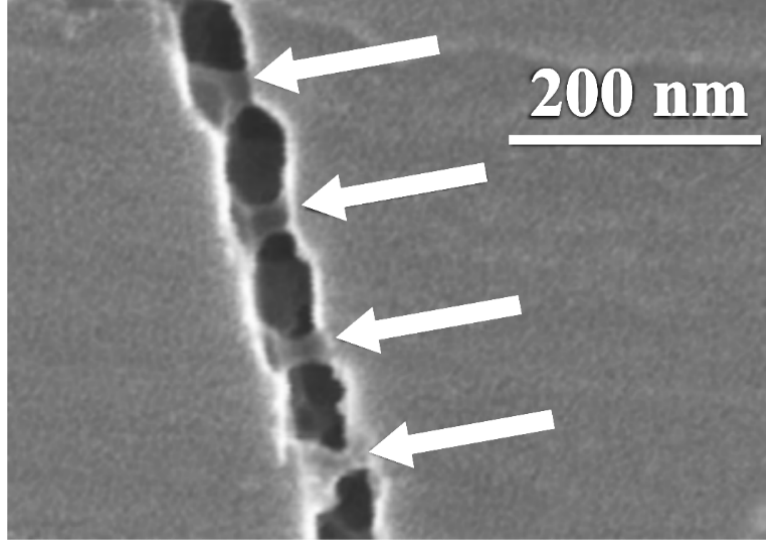


Figure 1.23: SEM image of observed fiber bridging toughening in CNT reinforced Al_2O_3 composite. The fiber bridges are marked with arrows.

curs when cracks propagate transversely to the longitudinal directions of the fibers, and long fibers can restrict the crack from further opening as well as decrease the driving force of propagation. The existence of residual tension along the axial direction of the fibers downgrades the bridging effect. Becher et al. proposed the increase in fracture toughness at steady-state as follows:

$$E^* = \frac{E}{(1 - \nu^2)} \quad (1.7)$$

where σ_f is the fiber ultimate strength. E_c and E_f are the elastic modulus of composite and fiber, respectively. G_m is the initial strain energy release rate of the matrix, and G_i is a critical strain energy release rate of the interface, V_f is the fiber volume ratio, r is the fiber radius, and ν is Poisson's ratio.

Fiber pull-out

Fiber pull-out toughening on the fracture surface is the next-stage failure of fiber bridging toughening. This unique toughening mechanism, which exists only in fiber-reinforced (or whiskers-reinforced) composites with weak fiber-matrix interaction demonstrates a two-step

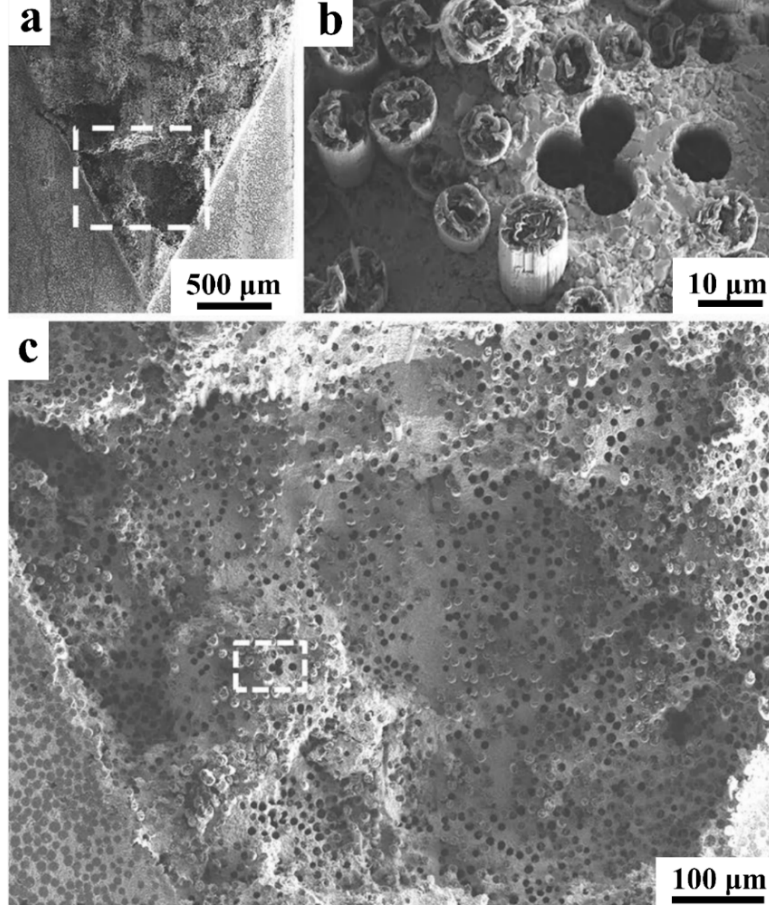


Figure 1.24: SEM images of fiber pull-out at the crack surface with (a) overall view of the crack surface, (b) magnified view from c, and (c) magnified view from a.

failure process: fiber debonding and fiber pull-out from the matrix. The work required to support debonding and overcome friction during the pull-out process at the fiber-matrix interface provides extra toughness to the macrostructure. According to Cantwell and Morton, the debonding and pull-out energies are expressed as:

$$W_d = \frac{\pi d^2 \sigma_f^2 l_d}{24 E_f} \quad (1.8)$$

$$W_p = \frac{\pi d \tau l_c^2}{24} \quad (1.9)$$

where, d is the fiber diameter, σ_f is the fiber failure strength, l_d and $l_c = \sigma_f d / 2\tau$ are the debonding zone length and critical transfer length, respectively, and τ is the friction constant

of shear stress.

1.2.6 PDC Energy Storage Applications

As mentioned in the previous section, PDCs are a unique group of compounds whose properties can be suitably tailored based on the composition of the preceramic polymer and processing parameters (temperature, gas environment, etc). As such, these materials offer a wide range of parameters that can be engineered to obtain electrochemical properties desirable for metal-ion batteries or supercapacitor systems. For example, negligible capacity fading at high current for LIBs is attained in PDCs that are carbon-rich and contain silicon mixed bonds; large-sized Na^+ ions could be accommodated in low-density amorphous PDCs via adsorption in micro-/nanovoids and the disordered carbon phase; ultra-fast charge and discharge is demonstrated in carbon-rich PDCs and nanocomposites in aqueous supercapacitor devices. In addition, there seems to be progress being made gradually in studying PDC-derived thin films and nanomaterials, which will provide more enhanced properties than at the bulk scale. As more diverse ranges of PDC and PDC-based composite materials are starting to emerge, their application as battery and supercapacitor electrodes will further our understanding of important phenomenological information about reaction mechanisms. Also, greater control over the phase distribution during PDC synthesis will result in efficient utilization of the precursors so that maximum energy density can be obtained. It is hoped that these novel materials, with their suitable properties, will find applications in electrochemical energy storage in the years to come.

PDCs are starting to receive increasing attention because of their superior properties and high theoretical capacities. However, several challenges persist that must be overcome for widespread deployment of PDCs as electrodes in energy storage systems-both batteries and supercapacitors. The relatively high cost of the pre-ceramic polymer precursor is an important concern; this cost is often more than that of battery-grade graphite, which is the negative electrode material in commercial LIB systems. Secondly, the processing temperature of PDCs is high ($\sim 1000\text{ }^\circ\text{C}$), which makes their fabrication an energy-intensive

process³⁸. Third of all, a high first cycle capacity loss, i.e. low first-cycle Coulombic efficiency is often a concern. Finally, PDCs also show a voltage hysteresis, indicating energy inefficiency³⁹. The outlook ahead lies in overcoming these obstacles, and considerable research is being pursued to achieve these objectives. PDCs, in general, provide high capacities- about ten times higher than graphite, if cycled at high current densities- and this can negate the higher cost over graphite to a large extent⁴⁰. Fine-tuning the synthesis so as to obtain the right phase/composition will lead to higher capacity and lower first cycle losses³⁹. Preliminary studies suggest large hysteresis losses can be reduced to some degree by cycling at low currents, but research in this area is still developing⁴¹.

The microstructure of PDCs essentially resembles a network of atoms similar in structure to graphene, with a network of sp^2 bonded carbon atoms located at the boundary of tetrahedral nanodomains of silica¹⁹. This is caused primarily by the limited solubility of carbon in silica. Increasing demand for superior properties of ceramics and rising challenges in engineering have accelerated the advancement of research and development in PDCs^{19;42}. Under these circumstances, recent analysis has shown several functional properties of PDCs to be eligible for application in electrochemical energy storage device^{43–46}. Figure 1.25(a) and (b) provide a schematic representation of the range of precursors and reaction paths that can be used to develop the requisite pre-ceramic polymers, along with their relevant properties. Figure 1.25(c) is a schematic of the types of bonds found in SiOC and SiCN PDCs. Several important properties of PDCs, especially those important regarding electrochemical energy storage devices, are discussed briefly below.

Chemical and thermodynamic stability

Chemical and thermodynamic stability is an important criterion for good electrode material. The electrode in a battery/supercapacitor is often subjected to corrosive environments and should be able to resist degradation in these regimes.

Chemical stability is a function of the bond strength of the different constituent elements in the PDC. Compared to conventional crystalline Si_3N_4 or SiC, polymer-derived SiCN ex-

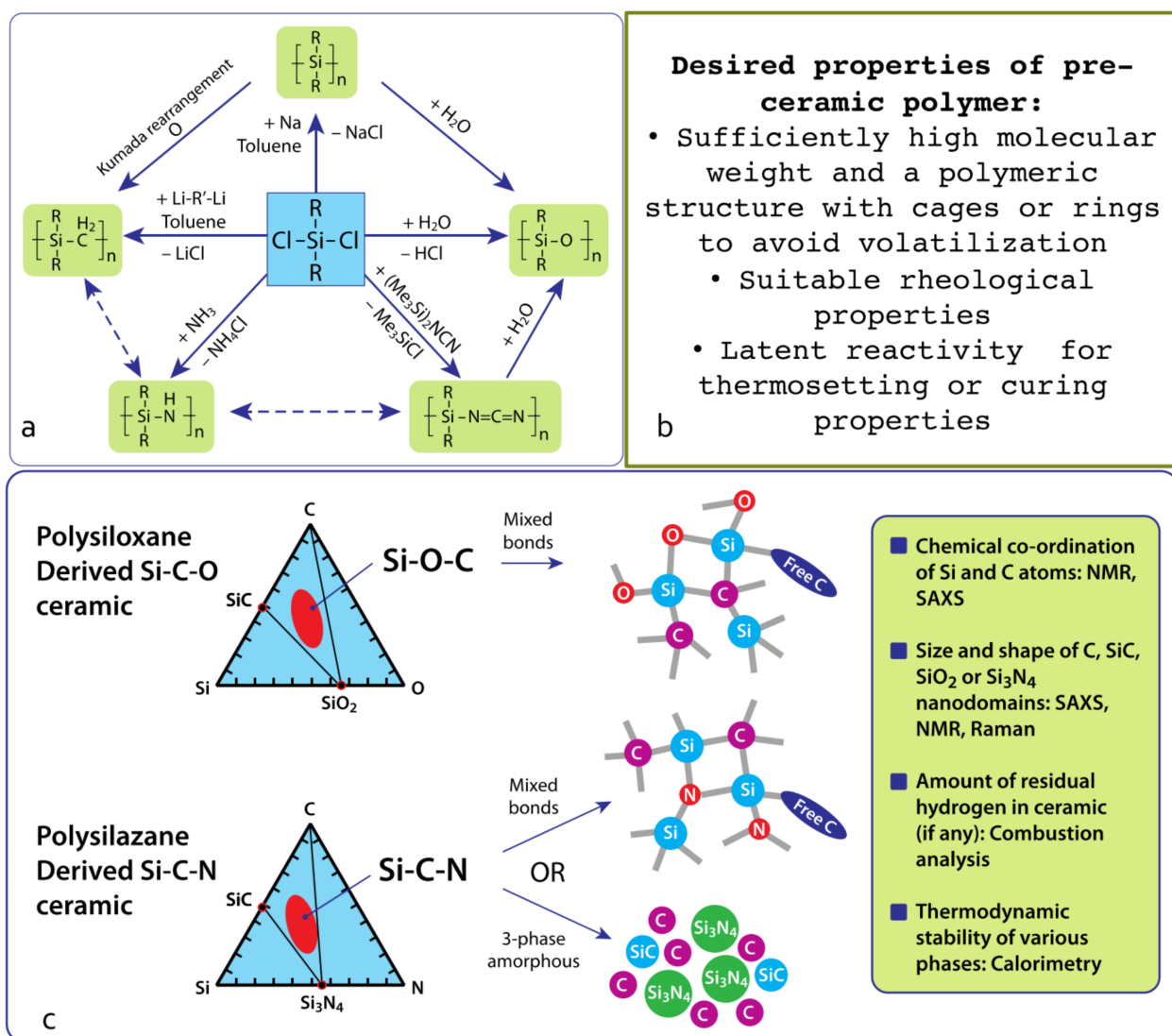


Figure 1.25: Structural property relations of the SiOC and SiCN systems. (a) Chloro-organosilicon compounds (generally obtained as by-products of the silicone industry) are low-cost precursors to pre-ceramic polymers. Reproduced from⁴⁷ with permission of The Royal Society of Chemistry. (b) Manufacturing of PDC ceramic fibers requires certain desired characteristics such as suitable rheological properties and latent reactivity. (c) Composition diagrams of polymer-derived SiOC and SiCN ceramics and schematic showing predicted corresponding atomic arrangements. The presence of nanodomains (e.g. SiC, SiO₂ or Si₃N₄, C) in PDCs is an intriguing feature of these materials. Reproduced from⁴⁸ with permission of The Royal Society of Chemistry. Because these ceramics are x-ray amorphous, structural characterization requires advanced techniques such as SAXS, EXELFS, XPS, and NMR.

hibits greater chemical stability owing to the existence of securely bonded Si-C and a lack of long term order in the ceramic structure^{49;50}. Nucleophilic reactions are prevented by the Si-C bond; additionally, the layered carbon network, which resembles graphene, largely

suppresses the diffusion of chemicals into these ceramics⁵¹.

Thermodynamically, PDCs with ternary systems (such as SiCN or SiOC) exhibit better stability than those with binary systems of the same elements, such as SiC, SiO₂, and Si₃N₄⁴⁷. The graphene network of insoluble free carbon formed at the silicon tetrahedral interdomain reduces the mobility of atoms, resulting in limited crystallization even at high-temperatures⁴³. With regard to the composition of PDCs, higher carbon content generally leads to a more amorphous structure. For example, in SiOC based PDCs, the free C phase prevents quick crystallization by hindering the mobility of atoms whereas, in SiCN systems, the graphene analogous network of C atoms forms a net-like structure around the Si₃N₄ nanodomains, thereby limiting nitrogen diffusion⁴⁸. Crystallization and decomposition resistance at a high-temperature can also be enhanced by the incorporation of elements such as B, Hf, and Zr⁵². The thermal stability of SiBCN ceramic is again improved from its parent SiCN since the doping of boron creates a turbostratic structure of the B-C-N phase that further reduces diffusion between domains⁵³. In conclusion, both regulations of processing parameters and better selection of doping elements can result in more thermodynamically stable PDCs¹³.

Electrical conductivity

The semiconducting or insulating behavior of a PDC is strongly influenced by its pyrolysis temperature⁵⁴. Electrical conductivity normally rises with the increase of pyrolysis temperature in accordance with increased percentage of carbon phase⁵⁴. DC-conductivities published recently for PDCs pyrolyzed at relatively lower temperatures (between 600 °C - 800 °C) demonstrates a change within the limit of 10^{-10} - $10^{-8} \Omega^{-1} \text{cm}^{-1}$ ^{16;54-56}. It has been observed that semi-conductivities (10^{-4} - $10^2 \Omega^{-1} \text{cm}^{-1}$) or even higher conductivities ($\sim 10^4 \Omega^{-1} \text{cm}^{-1}$) are observed for PDCs sintered at about 1000 °C - 1400 °C, due to the establishment of percolation networks of carbon⁵⁴. It is possible for PDCs pyrolyzed at temperatures higher than 1400 °C to obtain even higher electrical conductivities, due to the formation of nanocrystalline phases⁵⁵.

Processability

Conventional fabrication methods such as extrusion, injection molding, and hot/cold pressing, etc, can be used in developing PDCs. Moreover, processing complicated structures such as 1D fibers, 2D films and 3D shell/core nanocomposites is possible because of the ease of their polymer-to-ceramic processing route^{3;10;57–63}. Extraordinarily, a direct processing polymer-to-ceramic approach enables achieving uniformly distributed microstructure⁶⁴. The porosity of the PDCs is manipulated by either changing processing parameters-such as by introducing additives, altering pyrolysis temperature and atmosphere, or applying different processing strategies-such as templating, etching, blowing, decomposition, aerogels, and spinning⁶⁵. It has been reported by Vakifahmetoglu et al that porous PDCs can have a specific surface area up to $3000 \text{ m}^2 \text{ g}^{-1}$ with volumetric porosity of 15 - 96% and pore size of approximately 1 - 1.5 μm ⁶⁵. Erb and Lu have demonstrated the possibility of obtaining PDCs with varying porosity and ceramic content based on the presence of vinyl bonds in the precursor polymers⁶⁶.

PDCs as anode in LIBs

A significant amount of scientific research on silicon-based nanomaterials has been carried out, especially as negative electrodes for electrochemical energy storage devices, owing to silicon's favorable properties^{67;68}. Specifically, Si's ability to form a binary system with Li leads to a high theoretical energy density up to 4200 mAh g^{-1} , which is an order of magnitude greater than commercial graphite anodes in Li-ion batteries, as well as less potential in discharge^{69–72}. However, the primary drawback of Si is that the material may experience volumetric changes of up to 400 % on lithiation and delithiation, which results in electrode pulverization and considerable capacity fading⁷³.

One way of overcoming this problem has been to use silicon-based PDCs and not the silicon in its pure elemental form. Silicon-based porous PDC anode materials have been investigated with favorable outcomes to this end. Literature/the current state-of-the-art demonstrates that amorphous PDCs can reversibly store lithium within the voltage boundary

between 0.0 - 3.0 V while providing promising electrochemical capacity up to 900 mAh g⁻¹, as well as coulombic efficiency (CE) surpassing 99%. Other advantages of PDCs lie in their open amorphous but the thermodynamically stable structure and processability. However, their characteristic first cycle loss (a composition-dependent 27 - 50% loss) and hysteresis at a potential window of 0.8 - 1.2 V are issues that still need to be overcome. Modification of the pre-ceramic polymer's structure to achieve elevated surface area (porosity) and the addition of electrochemically favorable conducting nanofillers are some of the solutions that have been proposed.

For application as an electrode material, plenty of effort has been devoted mainly to the following two systems: SiOC, derived from polysiloxane, and SiCN, derived from polysilazane. While some drawbacks of these systems have been identified, researchers have focused on PDC based composites as well. The following sections will discuss the application and performance of these three types of PDC system as negative electrode materials in LIB systems.

The Si-C-O system is characterized by the presence of Si, C, and O atoms bonded together to form an amorphous structure⁷⁴. Free carbon, if present, prevents the crystallization of the silica phase. The network of the bonds and the free C content also control the oxidation resistance of the ceramic⁷⁴. The phase diagram of the Si-C-O ternary system is represented schematically in Figure 1.26. As can be observed from the figure, the light blue shaded zone is where the maximum capacity (solid red squares) region occurs, as SiO and SiC co-exist here with free C.

Bulk SiOC systems were first studied by Wilson et al when they conducted initial investigations on SiOC PDCs derived from polysiloxanes about their reversible lithium-ion insertion properties⁷⁶. They have successfully demonstrated capacities up to 600 mAh g⁻¹ within 1 V. Xing et al carried out a parametric study of 64 different SiOC samples with different chemical concentrations⁷⁵. They have demonstrated SiOC with 14% Si and 80% C to be the best commercially recommended material-over 25% Si, 45% C, and 30% O combination with higher reversible capacity and voltage hysteresis. Also, SiOC PDCs have performed better than crystalline SiO+C with equal Si, O, and C concentrations⁷⁵. Kaspar et al carried out

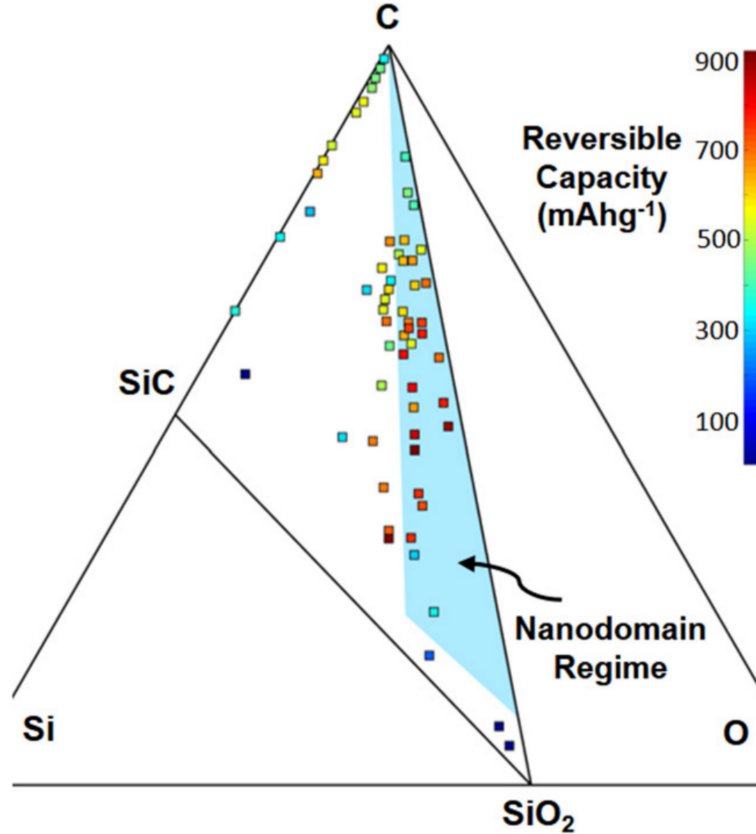


Figure 1.26: The Si-O-C phase diagram. The phase diagram of the Si-O-C ternary system, the shaded area towards the center of the ‘pyramid’ represents the tetrahedral ceramic phase consisting of mixed bonds and consisting of nanodomains. Reproduced with permission from ⁷⁵.

a study on polyorganosiloxane derived SiOC processed at temperatures ranging from 900 °C to 2000 °C⁷⁷. They have noticed a decrease in reversible capacity with increasing processing temperature (from 666 mAh g⁻¹ to 73 mAh g⁻¹ at current rate of 37 mA g⁻¹). Both XRD and FTIR results indicated the amorphous structure of samples pyrolyzed below 1200 °C, while additional SiC domains formed continuously at higher temperature⁷⁸. By mixing hydrogen with argon, Pradeep et al studied the impact of pyrolysis atmosphere on SiOC composition and its electrochemical performance⁷⁹. They observed that 5% of H₂ caused significant reduction in C concentration 55.15 wt.% to 46.37 wt.%; however, it elevated first cycle capacity (from 568 to 704 mAh g⁻¹) and efficiency (from 63 to 67%)⁷⁹. Additionally, Ahn et al focused their investigation on the significant hysteresis in SiOC as anode material in Li-ion batteries. They used a coulometric titration technique for this purpose and have demon-

strated hysteresis at a polarization potential of 250 - 500 mV⁴¹. This was attributed to the interface between anode and electrolyte, where the potential grows with increasing cycling⁴¹. From the measurement, the hysteresis was found to be a product of both thermodynamic limitations and kinetics of Li-ion diffusion between the different electrochemical potentials of Li-ions at SiOC-electrolyte and lithium-electrolyte surfaces⁴¹. Further measurement by Ahn et al was extended to the pre-ceramic polymer precursor chemistry with a variable composition of N and O in a SiOCN quaternary system⁴⁰. Results have shown far better performance in O-rich while very poor capacity for Ni-rich samples, where capacity changes rapidly with the dominant element near the ratio of N/O = 1. It has also been demonstrated that the SiOC structure is more stable than SiCN under the same conditions⁴⁰. Stronger covalent bonding in tetrahedral Si-N resulted in low efficiency in Li-ion binding and electron density localization than bonds in Si-O nanostructure⁴⁰. Approximately 100% capacity is recovered after 60 cycles for samples pyrolyzed at 800 °C and 1000 °C, compared to the significant drop for samples pyrolyzed at 1200 °C and 1400 °C⁴⁰. Fukui et al have studied the process of fabricating porous PDCs by increasing active surface area, which ultimately enhanced reversible capacity and cyclic performance^{80;81}. In their study, the blending of polystyrene and branched polysilanes was used to produce porous specimens having pore sizes of ~ 2 nm and surface areas of ~ 14 m² g⁻¹. The best reported result was a reversible capacity of 565 mAh g⁻¹ and 73% efficiency for SiO_{0.4}C_{0.8} ceramics^{80;81}. Li-ions have been demonstrated to be stored here in small quantities and in an ionized form. In a later work, they have also applied the microelectrode technique to SiOC single particles with a diameter of 13 μ m at 5 nA (4 C-rate) and have obtained 98% of coulombic efficiency after the first cycle, which shows strong agreement with porous electrodes⁸².

Thin-film SiOC anode materials have been studied on account of their flexible processing techniques⁸³. Experiments with SiOC films of 0.5 - 5 μ m thickness demonstrate performances comparable to bulk SiOC ceramics⁸³. SiOC thin films have the added advantage of being completely free from additives, which helps to reduce battery weight by significant amounts. The SiOC films showed reduced first cycle loss down to 27%, maintained capacity at about 1100 mAh g⁻¹ and approximately 99% of cycle efficiency⁸³. The authors have observed that

the thickness of the film influences the diffusivity of the Li ions⁸³.

The etching effect of KOH on SiOC anodes was specifically studied by Xia et al with various weight ratios (3:1, 5:1, 7:1) of KOH to vinyltriethoxysilane derived SiOC ceramics⁸⁴. Etched SiOC sample (with 5:1 weight ratio of KOH:pre-ceramic polymer) exhibited the highest specific surface area ($249.2 \text{ m}^2 \text{ g}^{-1}$) and reversible capacity (607 mAh g^{-1}) after 50 cycles, thereby revealing enhanced electrochemical properties with appropriate etching ratios. However, the authors have noted that high etchant concentrations may negatively affect the electrochemical performance due to the destruction of the free carbon phase⁸⁴.

The effect of electrolyte on the cyclability of the SiOC ceramic anode based LIBs have been carried out by Seko et al⁸⁵. As electrolytes, triglyme: G3 (Li(G3)TFSI) and tetraglyme: G4 (Li(G4)TFSI) have been used with various additives such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC). The highest initial capacity (1418 mAh g^{-1}) has been reported using Li(G4)TFSI without additives; however, lower capacity (1322 mAh g^{-1}) coupled with better cyclability (101% after 100 cycles) was obtained using Li(G4)TFSI with FEC⁸⁵. Therefore, according to Seko, ‘activation’ without additives is recommended to improve the initial capacity. Retention of capacity is then achievable via additives after the first cycle⁸⁵.

Li-ion insertion mechanisms have been studied by Liu et al, who carried out a series of characterization techniques (including ^{29}Si MAS NMR, Si XPS, and CV) for this purpose⁸⁸. The NMR, XPS, and CV were performed at three different stages (original, full lithiation, and complete delithiation) of SiOC samples, and SiO_2 and Si for comparison. The authors have noted four resonances to exist in the SiOC samples-namely, SiO_4 , SiO_3C , SiO_2C_2 and SiOC_3 -in which SiO_3C , SiO_2C_2 are electrochemically active to Li-ions dominating reversible capacity, while SiOC_3 is irreversibly converted into SiC_4 after the first cycle⁸⁸. A new insight has been proposed by Pradeep et al about the Li storage mechanism⁸⁹. The comparison between two sets of SiOC pyrolyzed at 1000°C and 1300°C revealed a composite-like behavior of $\text{SiC}_x\text{O}_{2(1-x)}$ glass phase and free carbon phase⁸⁹. Whereas $\text{SiC}_x\text{O}_{2(1-x)}$ provides a first insertion capacity as high as 1300 mAh g^{-1} , the cyclability and reversibility are dominated by free C⁸⁹. Fukui et al have analyzed the Li storage mechanism and first cycle loss in SiOC

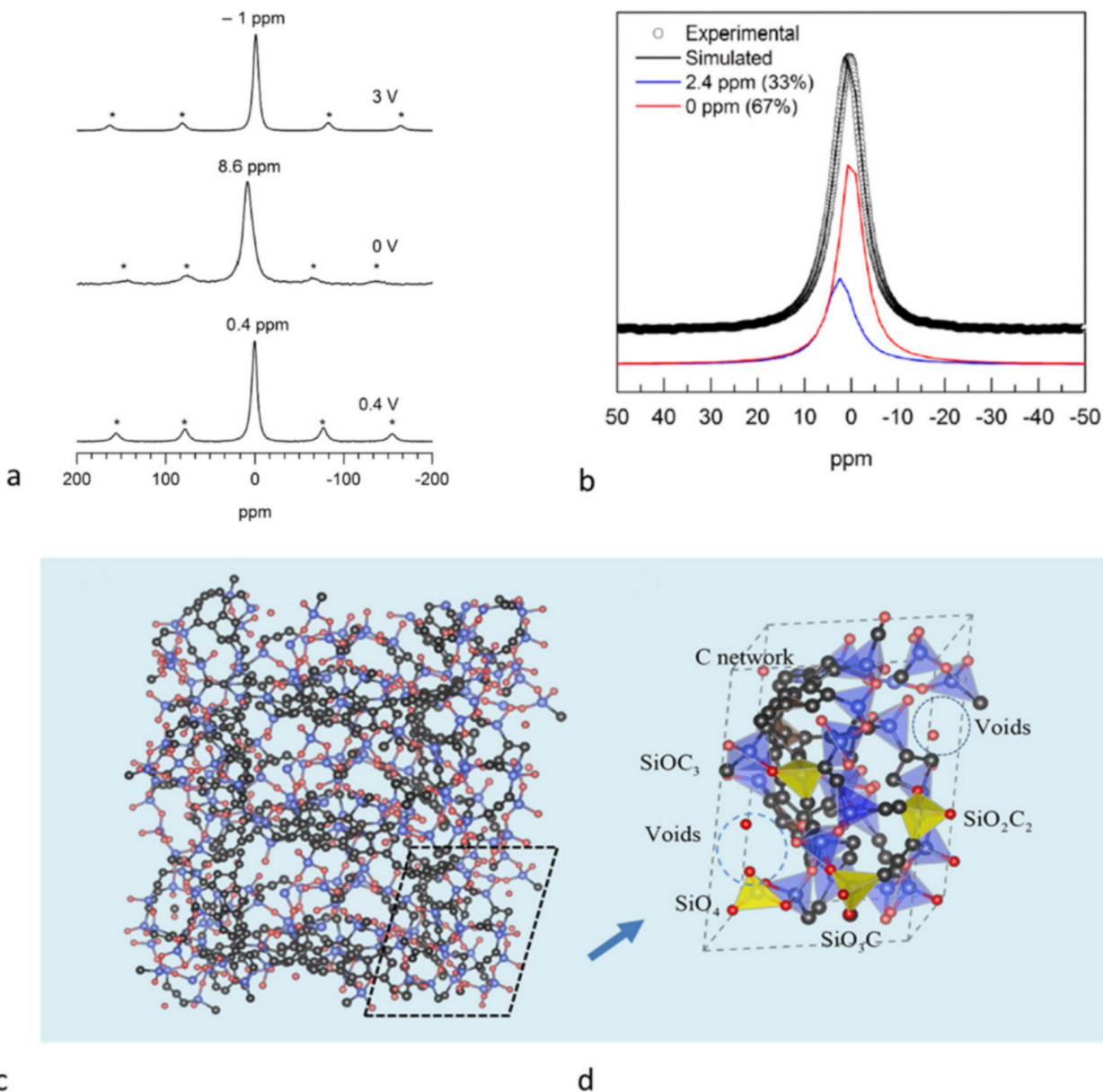


Figure 1.27: Understanding lithiation in SiOC. (a) Experimental ^7Li MAS NMR spectra of SiOC cycled between 0.005 - 3 V, lithiation up to 0 V and partial lithiation to 0.4 V, from top to bottom respectively⁸⁶. (b) Experimental and simulation comparison of the ^7Li MAS NMR spectra of the SiOC sample which has undergone partial lithiation up to 0.4 V⁸⁶. Atomistic modeling: atomistic model of silicon oxycarbide. (c) Supercell with an applied periodic boundary condition⁸⁷. (d) Unit cell-vertexsharing Si tetrahedra, nanovoids (blue dotted circle), and segregated C phase (gray atoms) are clearly marked⁸⁷.

species⁸⁶. They have demonstrated that the nature of Li species stored is mostly ionic from the ^7Li MAS NMR spectra (Figure 1.27(a)), and that only 30% of Li is reversible when cycled

between 0.4 - 3.0 V⁸⁶. This ionic nature is seen in greater detail in Figure 1.27(b), which shows a SiOC resonance peak at almost 0 ppm⁸⁶. More recently, Zhao et al investigated electro-chemo-mechanical effects of lithiation in carbon-rich SiOC using the first-principles approach⁸⁷. Their research suggests that Li insertion in SiOC is a two-step process: the Li is first absorbed in the nanovoids; this is followed by Li accommodation in SiOC tetrahedral units, free C atoms, and topological defects in and around the carbon network. The SiOC expanded by approx. 22% in the volumetric strain at its full lithiation capacity and the surrounding carbon network improved the structural stability of the SiOC lattice⁸⁷. The schematic of this process is depicted in Figure 1.27(c) and (d).

The Si-C-N system is obtained from polysilazanes and consists of C and N rich nanodomains if the pyrolysis is at low temperature; however, high-temperature pyrolysis results in the formation of Si₃N₄ and SiC rich regions instead⁹⁰. The phase diagram schematic is shown in Figure 1.28.

Bulk SiCN systems were studied by Liebau-Kunzmann et al who were among the earliest to suggest the possibility of applying SiCN PDC based electrodes in lithium-ion batteries⁹². In their study, Li-containing SiCN PDCs were synthesized at 1100 °C, and subsequent characterization showed the preferential formation of Li-N bonds during lithiation, indicating a potential for anode application⁹².

Temperature dependent electrochemical properties of SiCN PDCs for anode application have been studied by Su et al⁹³. It has been shown that samples synthesized at 1000 - 1300 °C showed the most favorable first reversible capacity up to 754.9 mAh g⁻¹⁹³. The authors have also demonstrated that fabrication temperatures any higher or lower provide significantly lower capacities, just in excess of 100 mAh g⁻¹. They have attributed this to remnant organics under 800 °C and crystalline SiC formed above 1400 °C, both of which blocked the path for efficient Li ion intercalation and storage⁹³. In addition, study on lithiation into carbon-rich SiCN derived by poly-diphenyl-silyl-carbodiimide has been performed by Kaspar et al specifically at the temperatures of 1100 °C, 1300 °C and 1700 °C^{94;95}. Among these additive free samples, the one synthesized at 1300 °C performed the best, demonstrating 383 mAh g⁻¹ reversible capacity and 69% coulombic efficiency and confirming that the free

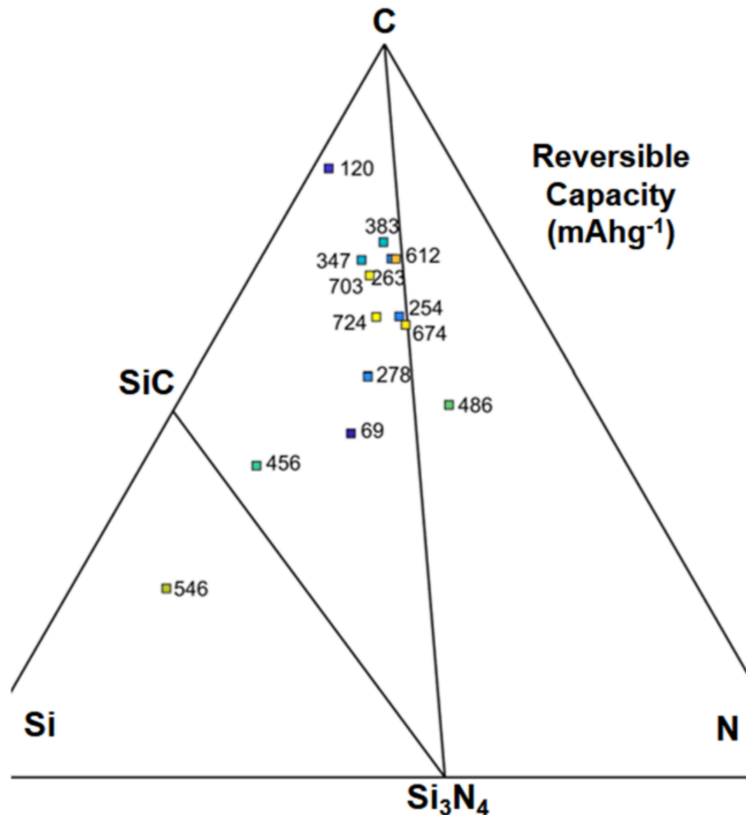


Figure 1.28: The phase diagram of the Si-C-N ternary system; once again, the maximum capacity regime occurs towards the center of the pyramid, where the Si_3N_4 and SiC phases coexist⁹¹.

carbon phase provides enhanced electrochemical performance by making more active sites available^{94;95}.

Molecular structure of pre-ceramic polymer's effects on electrochemical properties have been studied by Reinold et al⁹⁶. Different classes of pre-ceramic polymer- namely, polysilazane and poly-silyl-carbodiimide-were processed under the same conditions (1100 °C, Ar) revealing higher reversible capacities of 724 mAh g^{-1} and 612 mAh g^{-1} respectively⁹⁶. Similarly, coulombic efficiency of 89% to 61% (after 134 cycles), correspondingly for polysilazane derived ceramics and poly-silyl-carbodiimide derived ceramics were obtained, showing the consistently superior performance of the polysilazane pre-ceramic polymer⁹⁶.

Variation of pyrolysis environment on SiCN's performance as an electrode has been studied by Liu et al⁹⁷. A variation in the pyrolysis atmosphere from Ar to H_2 demonstrated higher constituent C content and a higher reversible capacity⁹⁷. Additional free carbon

source from divinylbenzene (DVB) has been shown to further increase the carbon content (from 9.9 wt.% to 49.3 wt.%) and specific capacity (from 136 mAh g⁻¹ to 574 mAh g⁻¹), while providing slightly increased hysteresis under 1 V⁹⁷. To further improve the electrochemical performance, heat treatment has been applied to poly silyl-ethylenediamine derived SiCN (SiN_{0.31}C_{0.97}H_{0.31}O_{0.05}) under 1000 °C in argon by Feng, resulting in the formation of nano-voids on the surface as well as enriched free carbon phase⁹⁸. The analysis indicated improved reversible capacity (above 300 mAh g⁻¹) even at high current (80 and 160 mA g⁻¹) for treated SiCN (SiN_{0.18}C_{0.41}H_{0.91}O_{0.10})⁹⁸. The enhancement was generally due to decrease of N content and increased O contamination during the heattreatment⁴¹. In general, the lithium intersection capacity of SiCN PDCs is strongly determined by the formation of amorphous graphene phase and nano-voids in the structure.

The capacity fading mechanism of SiCN was recently studied by Feng et al employing five different poly-silyl-carbodiimides as pre-ceramic precursor⁹⁹. They concluded that stable SEI layers formed on the surfaces of anodes prevent fracture of active materials during cycling⁹⁹. Besides, more carbon phase improves electrochemical conductivity and enhances the reactive sites in SiCN anodes. Therefore, the di-n-octyldichlorosilane (DODCS) synthesized poly-silyl-carbodiimide sample, containing the highest carbon composition, resulted in the highest reversible capacity of 826.7 mAh g⁻¹ after 100 cycles with coulombic efficiency above 97%⁹⁹. A comparison of the electrochemical performance of SiCN and SiOC is provided in Figure 1.29 along with SiOC's performance as a function of pyrolysis temperature.

PDCs as electrodes in supercapacitors

Supercapacitors are necessary where the power requirement predominates the energy requirement and it is necessary that charge is stored at or near the surface of the electrode materials. They are usually not constrained by ionic diffusion kinetics experienced in batteries and can run for a large number of cycles ($\sim 10^6$) at high charge and discharge currents. Therefore, the choice of appropriate electrode materials is necessary for their efficient performance, which necessitates the study of PDC electrodes.

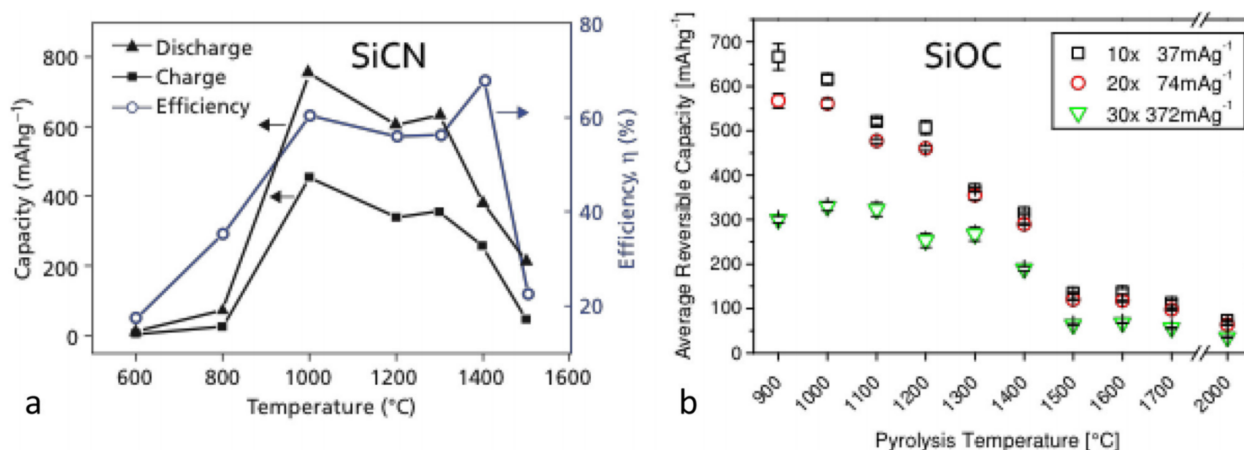


Figure 1.29: Comparative electrochemical performance of SiOC and SiCN with respect to pyrolysis temperature. (a) Comparison of electrochemical performance (charge and discharge capacities, efficiency) of SiCN specimens pyrolyzed at increasing temperatures⁹³. (b) SiOC average reversible capacity in dependence of temperature of pyrolysis. Average values were calculated from ten cycles¹⁰⁰.

SiOC electrodes in supercapacitors have been studied by several groups. SiOC with low carbon content has been studied by Halim et al¹⁰¹. Fabrication of the low carbon SiOC was performed by pyrolysis of silicone oil in an inert environment at various temperatures (700 - 1000 °C in steps of 100 °C)¹⁰¹. Detailed structural characterization by XRD and TEM have revealed an amorphous nature corresponding to the Si-O-C glass structure. Electrochemically, it exhibits a pseudocapacitive behavior providing an energy density as high as 25 W h kg⁻¹ with 98.7% capacity retention over 40000 cycles¹⁰¹. Oxygen functionalized high surface area silicon carbide flakes have been studied by Kim and co-workers¹⁰². The SiC was prepared by a one-step carbonization process followed by an H₂O₂ treatment to introduce surface-functionalized oxygen groups¹⁰². Specific capacitances of 243.3 F g⁻¹ have been obtained at scan rates of 5 mV s⁻¹ with 85.6% capacitance retention¹⁰³.

SiCN based electrodes have also received attention in supercapacitor applications. Si(B)CN-CNT and SiCN-CNT composites coupled with reduced graphene oxide (rGO) as electrodes in supercapacitors have been studied by David et al¹⁰⁴. The PDC composites were fabricated by chemical interfacing of pre-ceramic polymer with multi-walled CNTs, which were dispersed in sodium dodecylbenzene sulfonic acid (NaDDBS), in DI water¹⁰⁴. A specific capacitance of 269.52 F g⁻¹ at a current density of 5 A g⁻¹ was reported for the Si(B)CN-CNT-rGO

composite electrode.

SiOC as a precursor for developing nano and mesoporous carbon as electrodes in supercapacitors has also been analyzed^{105–107}. The carbon powders were obtained by mechanical milling of the SiOC precursor followed by subjecting it to chlorine treatment in an evacuated tube at 900 °C followed by NH₃ treatment to remove residual chlorine. BET analysis and XRD have shown a decrease in particle size with pyrolysis temperatures greater than 1000 °C and crystalline C powders respectively with no presence of β -SiC impurity phases¹⁰⁵. Specific capacitance of 148 F g⁻¹ has been obtained, with capacitance retention of up to 94.3% after 2000 cycles at current densities of 1 A g⁻¹, in aqueous KOH electrolyte¹⁰⁵. Along similar lines, Tolosa et al obtained nanoporous carbon remove residual chlorine. BET analysis and XRD have shown a decrease in particle size with pyrolysis temperatures greater than 1000 °C and crystalline C powders respectively with no presence of β -SiC impurity phases. Specific capacitance of 148 F g⁻¹ has been obtained, with capacitance retention of up to 94.3% after 2000 cycles at current densities of 1 A g⁻¹, in aqueous KOH electrolyte¹⁰⁵. Electrochemical results have produced energy densities of 42 W h kg⁻¹ at a power density of 30 kW kg⁻¹¹⁰⁷. Pyrolysis and chlorination of xerogel based SiOC-precursor derived carbons for supercapacitor applications have been probed by Meier et al¹⁰⁸. They have been able to obtain carbon samples with porosities greater than 200 m² g⁻¹, and specific capacitances of up to 110 F g⁻¹ have been obtained in organic electrolytes¹⁰⁸. Table 7 summarizes some of the important results of using PDCs as electrodes in for supercapacitor applications, along with their pyrolysis temperatures.

Chapter 2

Experimental Setup and Engineering Parameters

Synthesis of PDC fibers typically begins with fiber spinning from sol-gel preceramic precursors, in which most of the polymeric fiber spinning processes require certain physical properties of the raw material, such as flowability or viscoelasticity. Preferably, raw materials should have one of the following features: (1) are intrinsically liquid, (2) can dissolve in a certain solvent and form a homogeneous solution, (3) can form molten liquid phase at elevated temperatures. Silicon-based preceramic polymers are organosilicon compounds, such as monomers, oligomers, or polymers. Fewer repeating units (i.e., monomers or oligomers with low molecular weight) in silicon compounds often leads to lower melting points (may stay as a liquid at room temperature) and viscosity.

The silicon compound used for this research was comprised of cyclic oligomers with low molecular weights ($< 500 \text{ g mol}^{-1}$), that were water-like (low viscosity and density of $\sim 1 \text{ g cm}^{-3}$) liquid at room temperature. Therefore, high molecular weight carbon-based linear polymers are introduced to the system, in order to meet the viscosity requirement ($> 10 \text{ Poise}$) for sol-gel fiber spinning. Linear polymers acted as fiber templates and silicon compounds were embedded into the rigid polymer environment. After heat-treatment, crosslinked silicon compounds solidified at the site, and linear polymers were removed (or

decomposed) with additional heat-treatments of the fibers.

Commercial ceramic fibers, such as SiC fibers, are mostly produced via melt spinning at the industrial scale. With stable and consistent spinning environments, kilo-meter long fibers can be produced using this technique. However, melt spinning requires fine-tuned properties of preceramic polymer precursor while it is a molten and long production line for the following crosslinking and pyrolysis. Hence, the melt spinning technique is neither suit for many other preceramic silicon precursors, nor an applicable setup for lab-scale production as well with high energy consumption.

2.0.1 Hand Spinning Setup and Engineering Parameters

The PAA aqueous solution initially was used to test if the spinning bench was functioning well, but then various quantities of liquid silicon compounds were introduced into the PAA sol-gel system to determine the maximum load that PAA could carry. The early stage of the hand spinning setup focused on the spinnability of the sol-gel system. The spinning setup was built for a simple massive drawing of continuous fibers as shown in Figure 2.1.

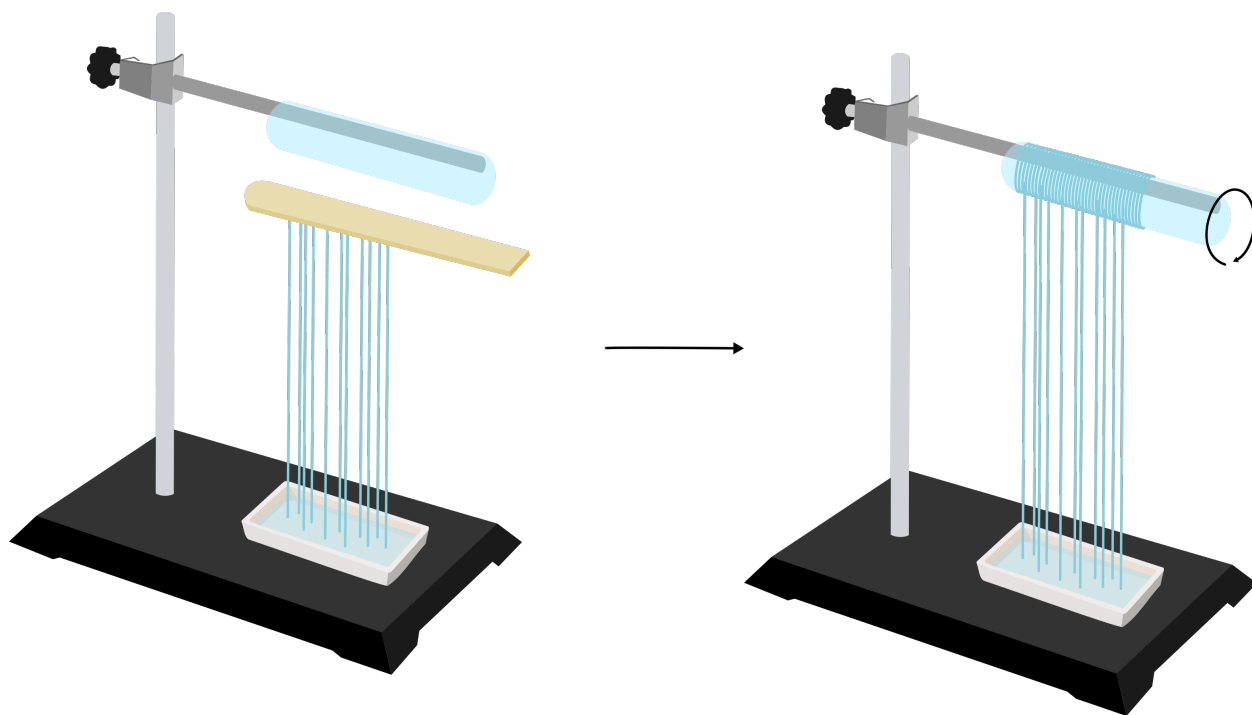


Figure 2.1: *Early stage hand spinning setup for continuous fiber roll production.*

Several continuous fibers could be simultaneously and continuously drawn from the sol-gel pool using a flat stick, such as metal pieces, glass rods, or wooden flat sticks (which showed the most promising performance). After fibers were drawn and attached to the collector, simply by rolling the collector, fibers were continuously rolled onto the glass collector and then can be collected as a complete fiber roll and processed in a low-temperature open-air oven for crosslinking. Final pyrolysis at elevated temperature in inert gas completed the final polymer-to-ceramic conversion of fiber rolls.

Key factors and parameters during the fiber spinning process included the following:

1. The loading amount of the silicon preceramic precursor drastically changed the viscoelasticity of the sol-gel due to the great morphological difference between the silicon oligomers and linear polymers. Increased precursor loading resulted in high ceramic yield after pyrolysis but also raises the difficulty of fiber drawing.
2. The initial concentration of PAA aqueous solution affected the viscoelastic properties of the fiber rigid environment (fiber template). A high polymer concentration led to high viscosity and, increased strength and elasticity during the fiber drawing process, resulting in thicker fibers but potentially harmful small beads at the fiber surface.
3. The height between the sol-gel pool and the fiber collector influenced the fiber morphologies. A large vertical distance resulted in thin fibers and narrow fiber diameter distribution due to uniform gravitational pulling during the fiber drawing process. However, high viscosity is required to increase the vertical distance.

Ceramic fiber rolls were successfully synthesized via hand spinning from the cyclic preceramic precursors/linear polymer hybrid systems. The objective was to draw long, straight individual fibers to evaluate the properties of handspun fibers with the highest ceramic precursor load. The second-stage hand spinning setup is shown in Figure 2.2.

Overall setup implementation was focused on individually drawing the fibers. As shown in the schematics, the sol-gel was prepared in the same way as the previous method, but, instead of drawing fibers onto the roller-like collector, fibers were individually drawn with a tweezer onto a hand-crafted aluminum boat. Fibers were hung between the boat walls to minimize fiber interaction. Because fibers were crosslinked on the boat, shrinkage during

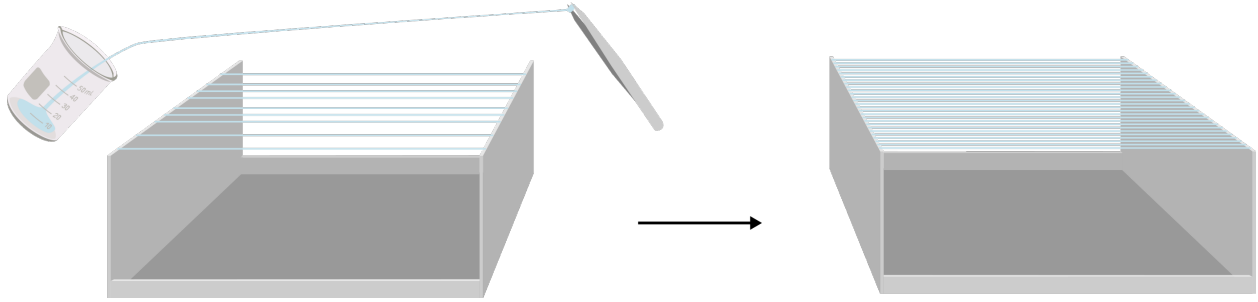


Figure 2.2: *Second stage hand spinning setup for continuous single fiber production.*

crosslinking provided uniform tension on each fiber and produced smooth, uniform fiber surface. Key factors and parameters included the following:

1. The boat size determined the length of the synthesized fibers; the size could be adjusted based on the size of the low-temperature oven for crosslinking.
2. Fiber drawing (or stretching) speed is directly controlled by hands, that determined the fiber diameter and the diameter distribution. The synthesized fibers could have diameters less than a micron meter.

2.0.2 Electrospinning

The electrospinning setup was established for the massive production of ceramic fibers at the lab-scale. The setup includes four major parts: a sol-gel feeding and extrusion system, a fiber collecting system, an Arduino UNO R3 control system, and a high-voltage power supply system, as shown in Figure 2.3. The extrusion system and collecting system were placed in a transparent acrylic box for safety and ease of cleaning.

Sol-gel feeding and extrusion system

The extrusion system consisted of a sol-gel container (10 ml syringe, may switch to other sizes as 5 ml or 20 ml), a corresponding syringe mount, a high-precision step motor, and a position sensor (optional). The final design is shown in Figure 2.4.

The NEMA 23 shown in Figure 2.4 was a bipolar stepper, selected for its high torque and precision controllability (200 steps per revolution). The stepper motor was preinstalled on a

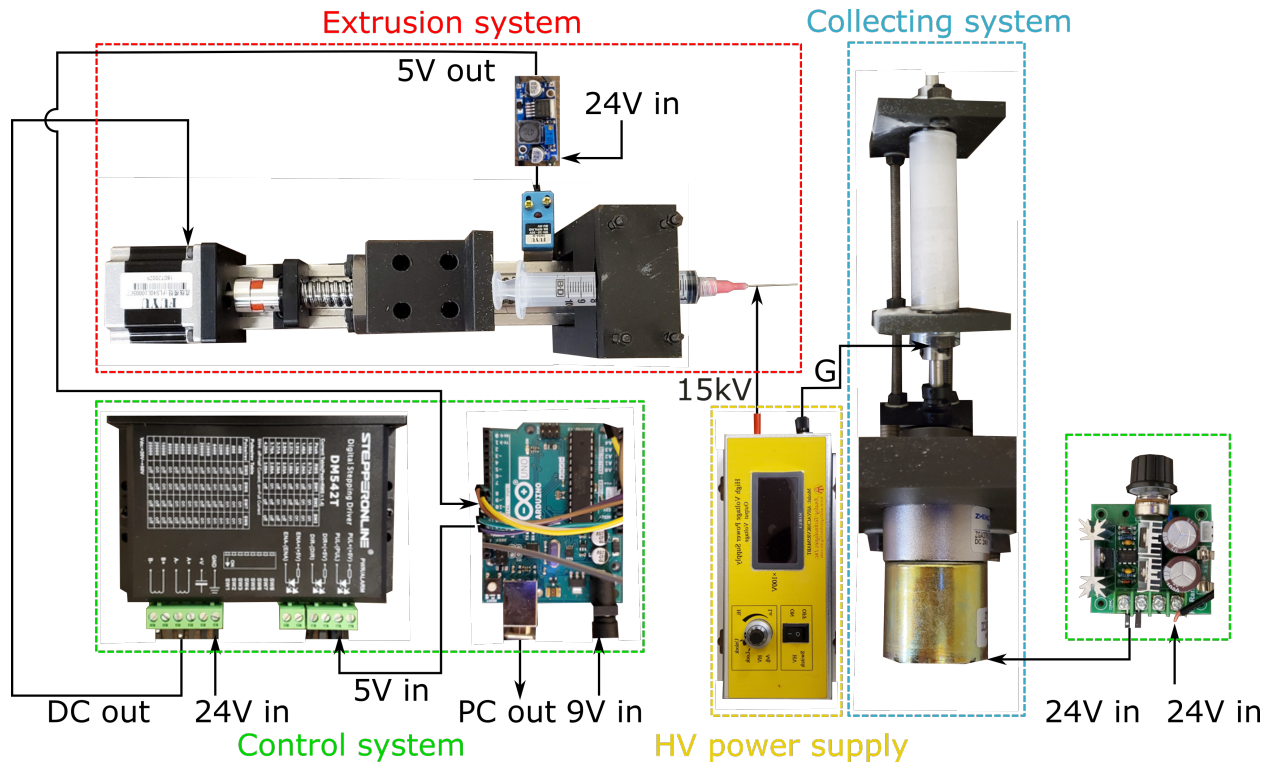


Figure 2.3: *Electrospinning setup for massive production of fiber mats.*

linear guide slide with a 100 mm stroke, directly connected to the 24 V stepper motor driver, and controlled by the Arduino. The sol-gel container, a 10 ml syringe, was mounted on the 100 mm stroke and preloaded with a spinning solution. The syringe mount parts were 3D printed via an FDM printer with high-strength nylon with 100 % solid fill to endure the high pressure from the stepper motor during spinning. Consequently, movement of the feeding stage was limited and controlled by the stepper motor; a late power cut or wrong rotating direction could cause internal damage to the stepper motor. A position sensor reversed the motor-rotating direction when the feeder reached the end of the slide, which also increased the automation of the extrusion system.

Fiber collecting system

The fiber collecting system included a high-torque/high-speed motor, metallic cylindrical current collector, and an outer frame to connect the motor and the current collector (Figure 2.5-6).

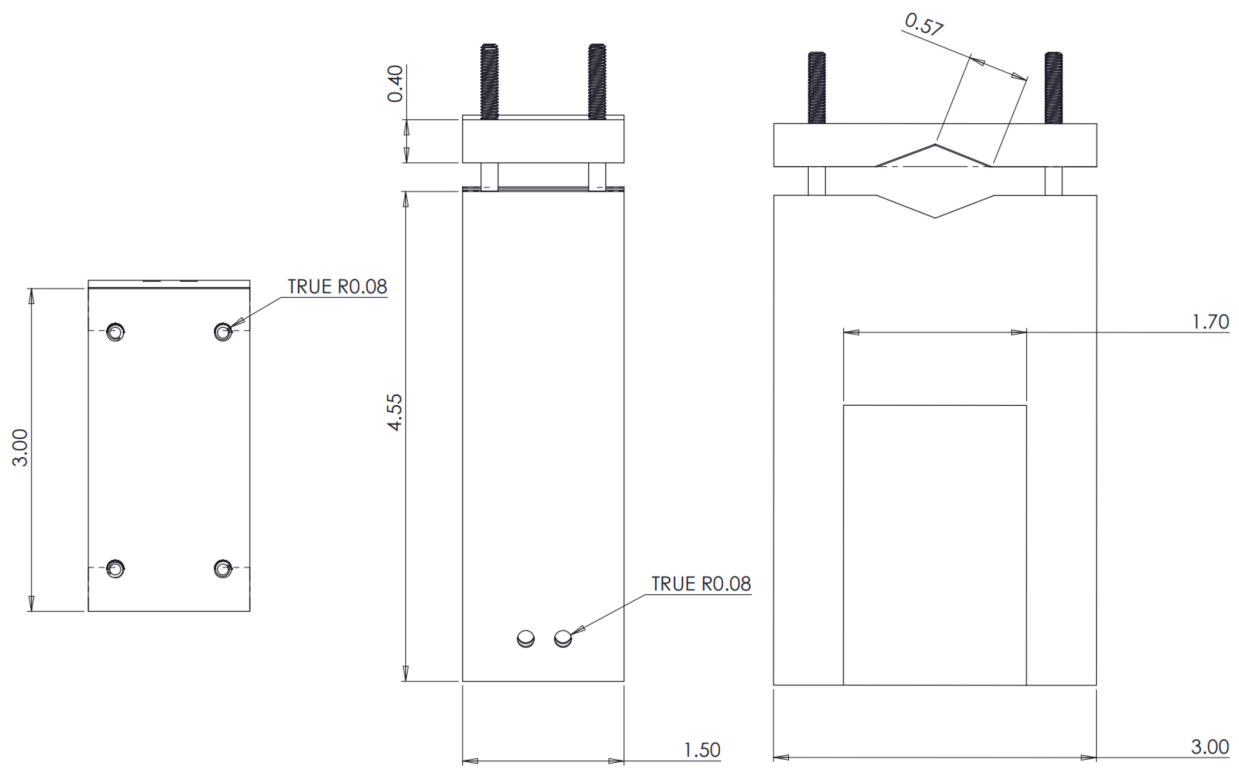


Figure 2.4: *Original design of extrusion system. (Unit: inch)*

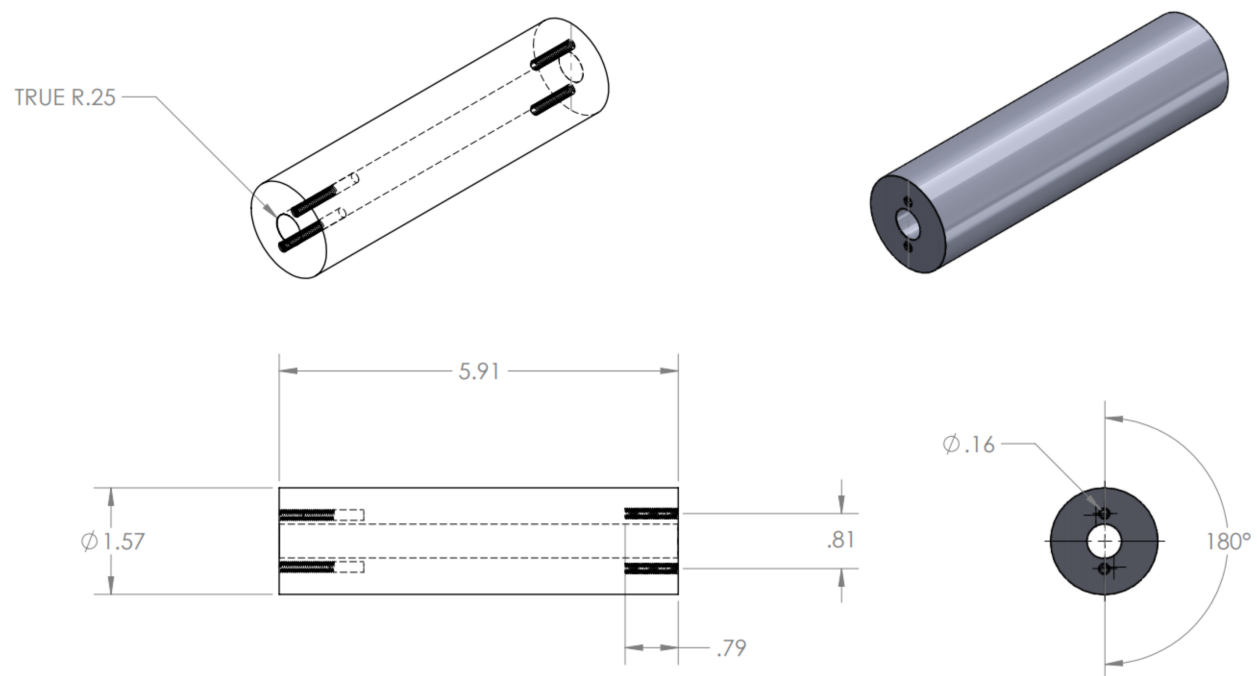


Figure 2.5: *Original design of current collector. (Unit: inch)*

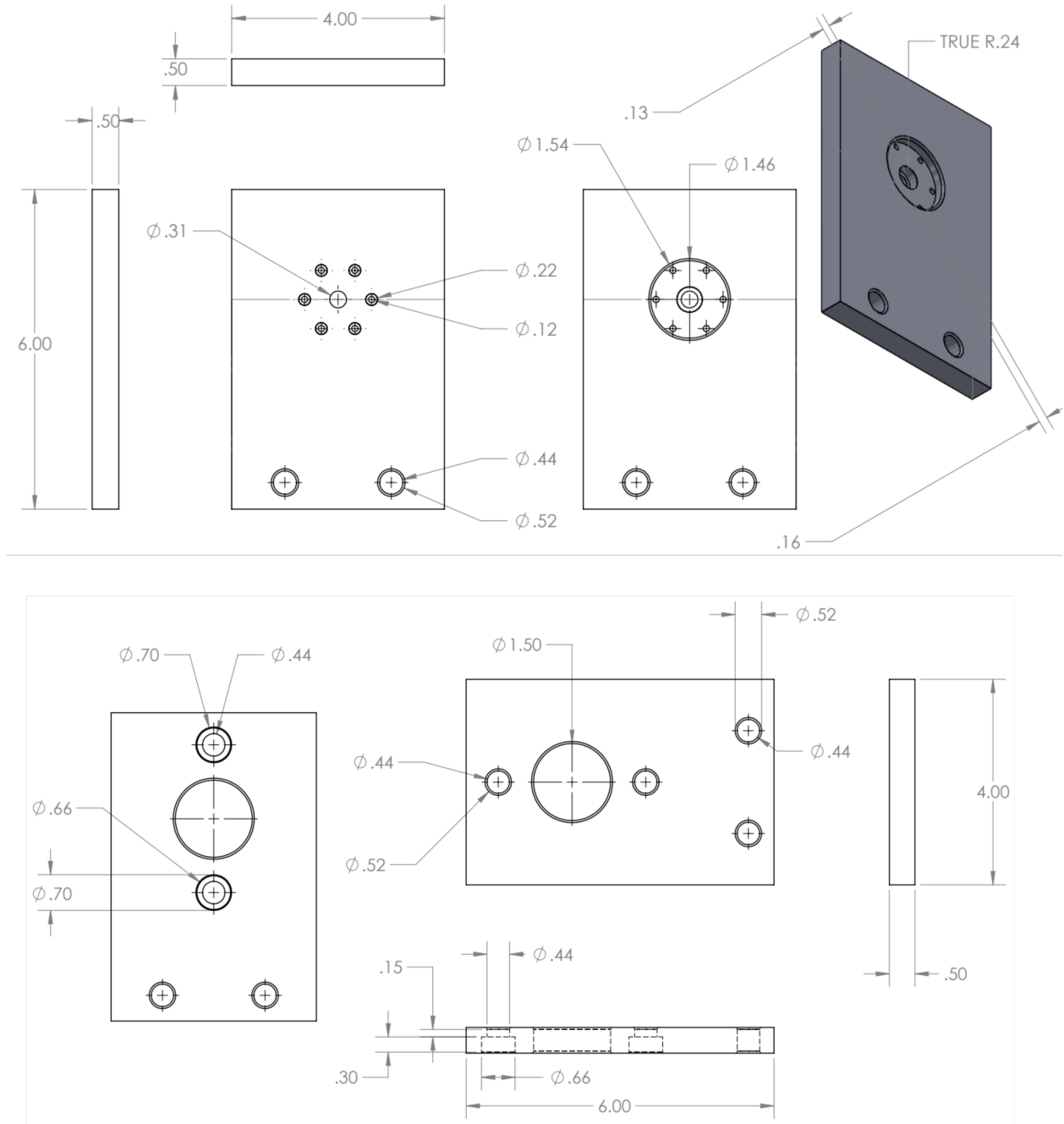


Figure 2.6: Original design of fiber collector frame. (Unit: inch)

An aluminum alloy cylinder was selected as the current collector because the aluminum alloy is relatively lighter and easier to machine than stainless steel. The current collector was machined to 15 cm in length and 4 cm as the outer diameter. During electrospinning, the current collector was covered with a layer of a conductive film (e.g., aluminum foil) to

control contamination from previous materials and to simplify the fiber mat separation and cleaning process after spinning. The resulting size of the fiber mats was approximately 15 cm by 12 cm. Rather than a direct connection between the motor and the current collector, a stainless-steel shaft was connected to the high-speed motor to better control the rotation center of mass. The rest of the shaft was mounted on the frame parts using several bearings to further stabilize the high-speed rotation. The motor was powered by another motor driver with built-in coarse speed control.

Arduino control system

The control system was comprised of an Arduino UNO R3 system, a stepper motor driver, a high-speed motor driver, and power supply, and a prototype printed circuit board (PCB), through which all other parts are connected as shown in Figure 2.7.

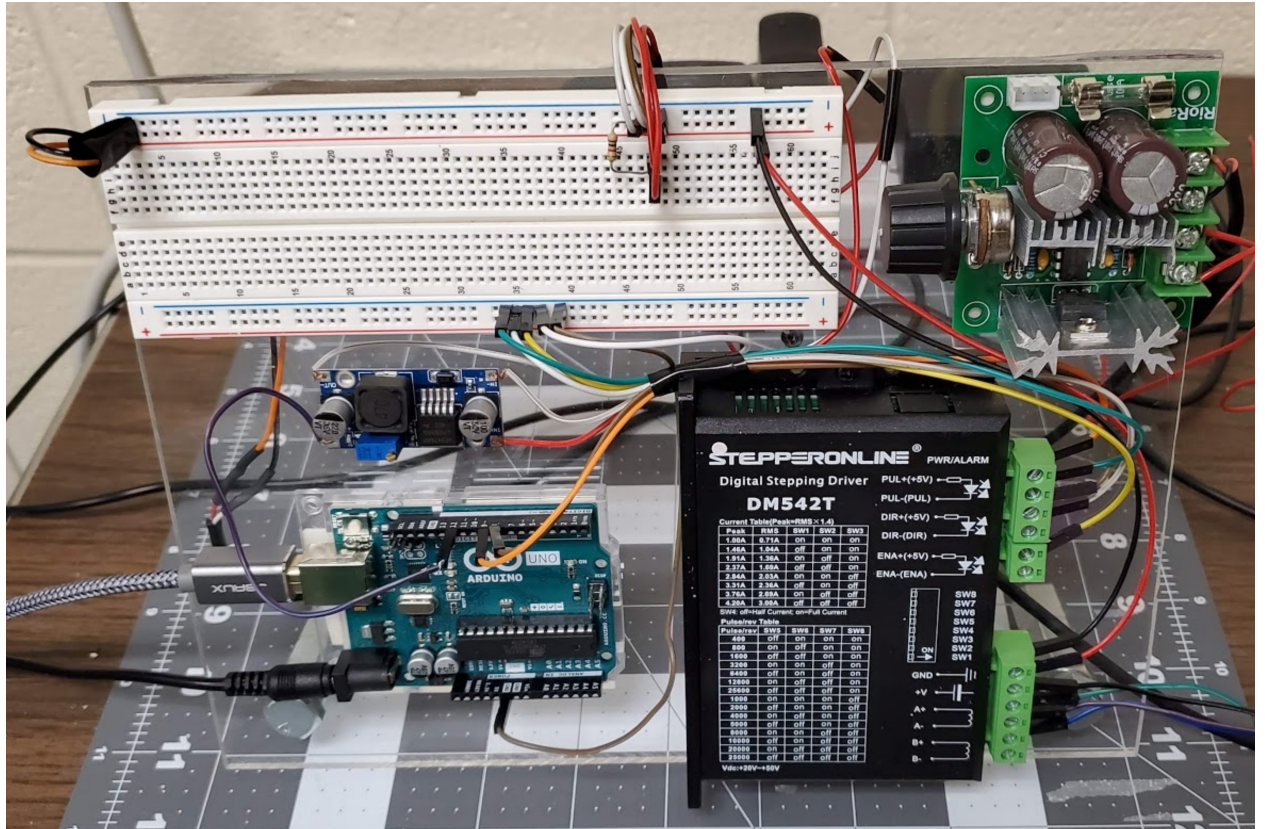


Figure 2.7: Camera image of Arduino control system setup.

The system was primarily built for precision control of the stepper motor that drives the

extrusion system. Arduino coding were used to define and precisely control motor step size and number of steps. The Arduino system continuously supported the signal and power to the stepper motor driver until the stage reached the farthest limit as detected by the position sensor. Then the Arduino system reversed the current supporting sequence to reverse the motor rotating direction until the stage returned to the beginning position.

High-voltage power supply system

A high-voltage power supply with a maximum of 30 kV DC output was purchased to establish the potential difference between the extrusion system and the current collector. The high voltage output was connected to the metallic needle tip of the extrusion system, and the ground output is connected to one of the bearings holding the shaft. The DC output was set to 15 kV to provide sufficient but stable potential.



Figure 2.8: *Image of high voltage power supply.*

Engineering parameters of electrospinning

Many factors determine if fibers form during an extrusion. Slight changes of the working parameter may lead to completely different fiber morphology (e.g., fiber diameter, diameter uniformity, surface feature, length, and mat amount on the aluminum foil) and may produce a film (or collapsed fibers) rather than individual fibers. The key factor for the spinning process was to ensure that the extruded sol-gel can convert from stable Ohmic flow to

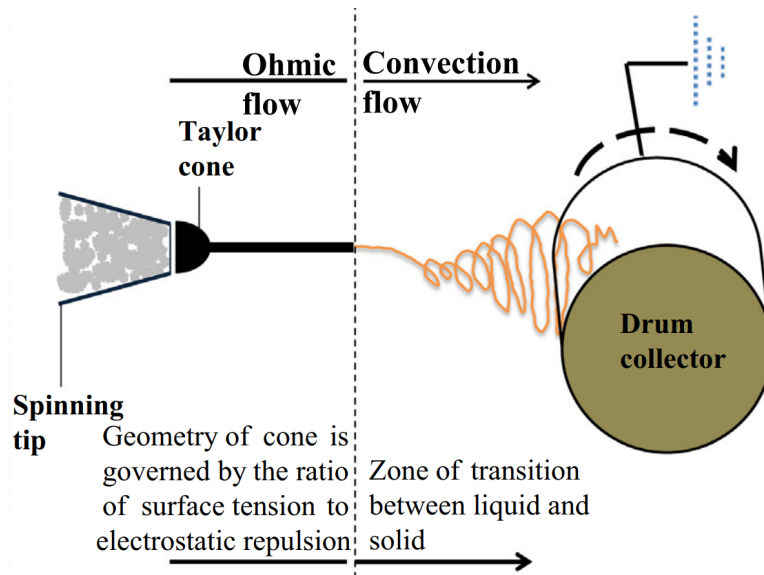


Figure 2.9: *Conversion of Ohmic flow to convection flow during electrospinning.*

convection flow. In the convection flow region, a stable liquid flow gets converted to solid fiber form by the evaporation of the solvent. The following factors were shown to affect fiber qualities:

1. Rotational speed of the stepper motor that directly controlled the pushing speed to the syringe. When the cross-sectional area of the syringe was fixed (fixed syringe capacity), the solution feeding speed was directly controlled only by the rotating speed of the motor. A faster feeding rate pushed more materials out of the needle tip but required a longer distance or higher voltage to separate the sol-gel into individual fibers. Hence, slow extrusion increased the flexibility of other factors. A series of test spinning also showed that a slow feeding rate with high step precision is preferred.
2. High voltage provided the drawing force at the surface of the sol-gel. Although the voltage must be high enough to motivate the bursting, an excessive-high voltage may cause fibers to be drawn to random spots rather than collected only on the fiber collector.
3. Distance between the needle tip and the fiber collector can be adjusted based on the voltage and feeding speed. This distance is typically more than 20 cm and may be adjusted if the fiber bursting point is too near to the fiber collector.
4. Air bubbles must be removed before mounting the syringe to prevent inconsistent

sol-gel flow during spinning.

Further detailed information and other parameters can be found in many previous research articles or reviews^{109–115}. Based on the existing guidance and trial runs, the optimized engineering parameters were selected. The detailed parameters are presented in Chapter. 5.

Chapter 3

Characterization of polymer-derived ceramic fibers

Polymer derived SiOC or SiCN ceramics have been shown to have nanodomain structures that exhibit heterogenetic properties at the nano-scale while demonstrating amorphous features under X-ray spectroscopy¹¹⁶. In 2007, Varga et al. found that silicon oxycarbide ($\text{Si}_x\text{O}_y\text{C}_z$) structure is a thermodynamically stable combination of crystalline silica (SiO_2), silicon carbide (SiC), and graphitic carbon¹¹⁷. The unique amorphous structures of PDCs are critical for ionic conductivity, crystallization, and nucleation. Although these structures also determine the mechanical (creep resistance) and thermal (oxidation or corrosion resistance) properties at high temperatures, they may experience crystallization and phase segregation with the release of gas products at temperatures above 1000 C¹³. Therefore, spectroscopic or microscopic investigations of these property-related nano-to-micron structures are essential for measuring and controlling the properties of synthesized PDCs.

Traditionally, techniques such as X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Fourier transform infrared analysis (FTIR) and nuclear magnetic resonance (NMR) are used to characterize PDC materials and expose their molecular structures. XRD, which reveals size information of crystal structures (at least 1-2 vol %) within the bulk material¹³, can confirm the amorphous structures of low-temperature

PDCs, or crystalline α -SiC, β -SiC, SiO₂, and Si₃N₄ of high-temperature PDC products, as well as the size of crystalline carbon phase, which forms at elevated temperatures.

Raman Spectroscopy

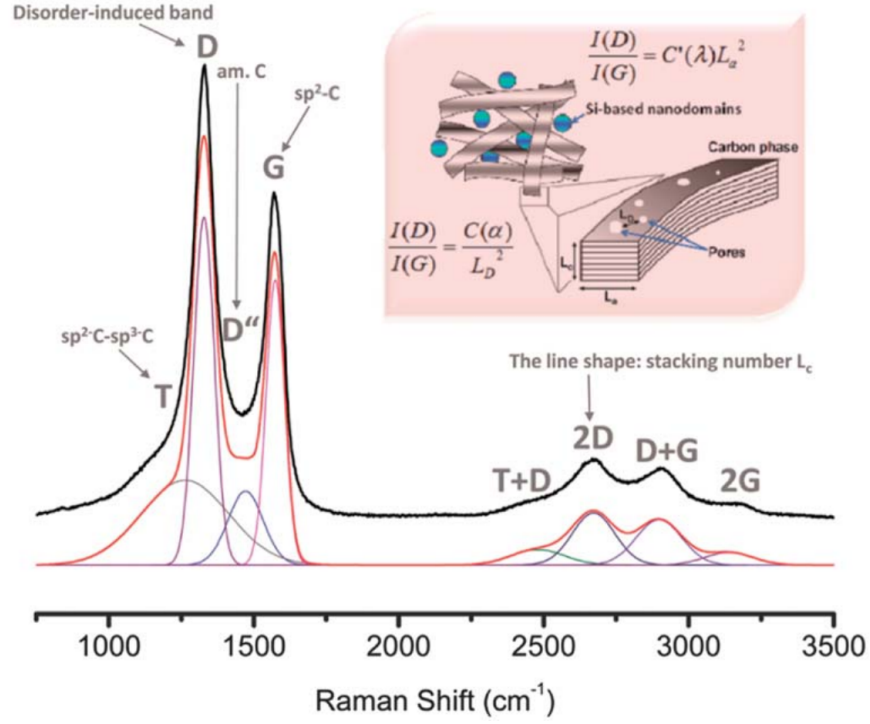


Figure 3.1: Raman spectroscopy of SiCN from poly(phenylvinylsilylcarbodiimide) with integrated peaks marked out.

Raman spectroscopy can effectively determine the free (or excessive) carbon phase of PDC structures. Depending on the power of the incident laser, the technique itself is a nondestructive, localized method that collects bulk information of a few microns on the sample surface. In SiOC or SiCN PDCs, the signals at $\sim 1350 \text{ cm}^{-1}$ and $\sim 1590 \text{ cm}^{-1}$ correspond to carbon “D” and “G” bands, where “D” is associated with disordered sp³ bonds and “G” is related to ordered sp² bonds (Figure 3.1)⁴⁸. Raman spectroscopy can also detect signals at $\sim 2950 \text{ cm}^{-1}$ from “D+G” combined mode, thereby providing information regarding the amount of free carbon and defects.

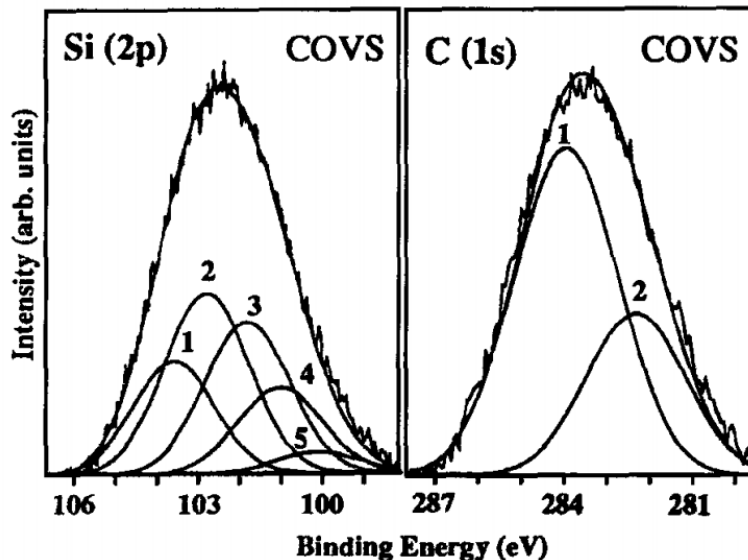


Figure 3.2: XPS spectra of SiOC. Left: integrated Si2p high resolution scan with peaks at (1) SiO_4 , (2) SiO_3C , (3) SiO_2C_2 , (4) SiOC_3 and (5) SiC_4 . Right: integrated C1s high resolution scan with peaks at (1) C-C and (2) C=O.

XPS

Similar to Raman spectroscopy, XPS is also a surface technique that gathers information from the sample surface. However, combining with proper ion etching, XPS can also obtain information from bulk after removing the surface layer. XPS survey scan is often used to provide information on the elemental composition of a target sample. Atomic percentages of each element are calculated directly from the area under the corresponding characteristic peaks. Besides, detailed bonding information of each element may be found from a high-resolution XPS scan. In the case of SiOC PDCs, silica tetrahedral microstructures, such as SiO_4 , SiO_3C , SiO_2C_2 , SiOC_3 and SiC_4 , can be identified from the integrated peaks of Si2p high-res peak (Figure 3.2)¹¹⁸. Similar bonding information regarding carbon elements, such as C-C, C=O, and C-Si, can be found via integrating C1s high-res peak.

Nuclear Magnetic Resonance

NMR spectra of selective elements in amorphous or crystalline PDCs provide highly sensitive, accurate structural information. For amorphous PDC materials, NMR can detect the

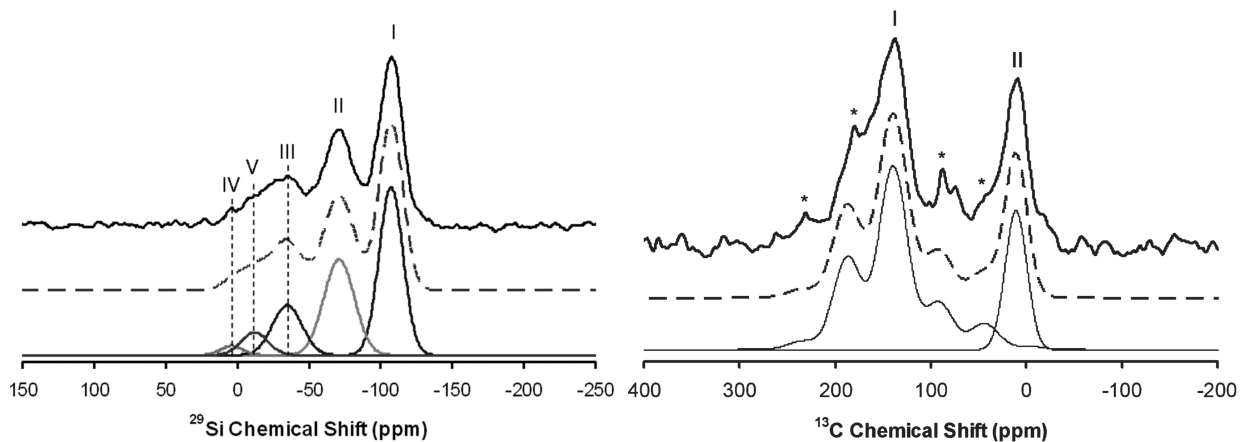


Figure 3.3: NMR MAS spectroscopy of ^{29}Si (left) and ^{13}C CP(right).

spatial distribution of certain nuclides in chemical environments and impurities or defects (dangling bonds) within the structure. For example, for SiOC derived from MK powder, ^{29}Si MAS NMR spectroscopy revealed five different silicon tetrahedrons at different chemical shifts (or energy levels): SiO_4 , SiO_3C , SiO_2C_2 , SiOC_3 , SiC_4 at -107, -71, -34, 7, -11 ppm¹¹⁹. The relative amount (at. %) of listed microstructures can be calculated by integrating the corresponding peaks, or areas under the curve. Similarly ^{13}C CP MAS showed two carbon environments in the SiOC PDC, where ~ 140 (with ~ 80 and ~ 180 ppm as spinning sidebands) and ~ 12 ppm corresponded to sp^2 graphite environment and sp^3 SiC environment, respectively.

BET

BET analysis may be beneficial to investigate surface or pore features of PDC fibers. By analyzing the BET adsorption and desorption curves, BET analysis is capable of providing BET surface area, micropore volume, and micropore size information. Also, different shapes of adsorption and desorption curves provide information on pore size and shape via different isotherm types and adsorption hysteresis, respectively¹²⁰.

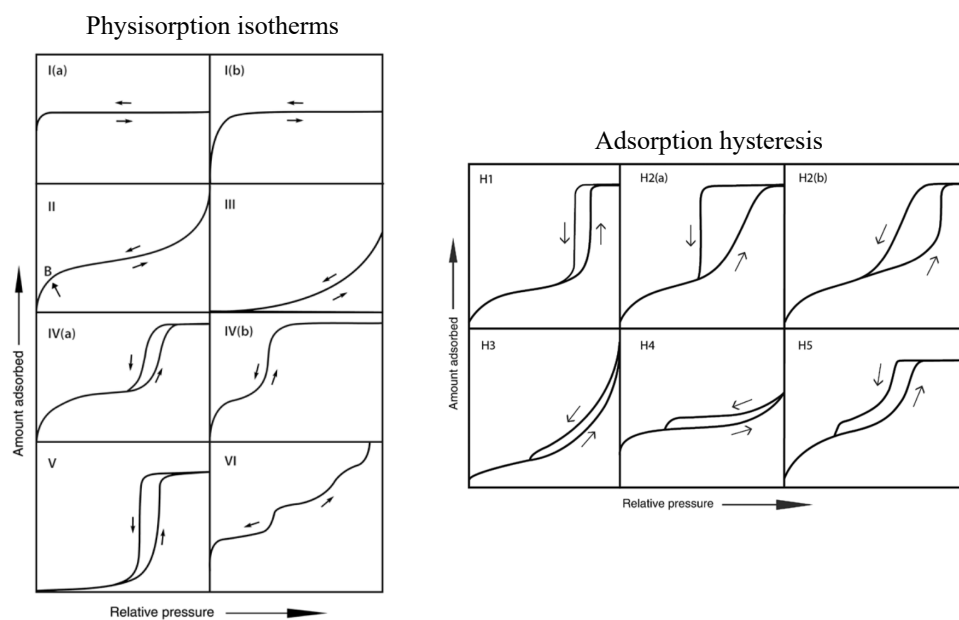


Figure 3.4: *Left: BET physisorption isotherms. Right: BET adsorption hysteresis.*

Chapter 4

Preparation and Structure of SiOCN Fibers Derived from Cyclic Silazane/PAA Hybrid Precursor

Overview

Ceramic matrix composite (CMC) materials have been considered a desired solution for lightweight and hightemperature applications. Simultaneously, among all different CMC reinforcements, polymer-derived ceramic (PDC) fibers have gained attention for the intrinsic thermal stability and mechanical strength with simple and cost-effective synthesis techniques. Here, carbon-rich SiOCN fibers were synthesized via hand-drawing and polymer pyrolysis of a hybrid precursor of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasilazane (TTCSZ) and poly-acrylic acid (PAA). The type of silazane reported in this work is considered as a major precursor for SiCN; however, it is unspinnable, due to its unfavourable physical properties (low viscosity) and chemical structure (cyclic rather than linear structure). The introduction of PAA to TTCSZ to create a hybrid precursor remarkably improved the spinnability of the silazane and should be widely applicable to other unspinnable PDC preceramic polymers. Investigations on the structural and compositional development of the fibers were mainly conducted via Raman spectroscopy, Fourier-transform infrared spectroscopy, scan-

ning electron microscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance and thermo-gravimetric analysis to determine spinnability, free carbon content, cross-linking and pyrolysis behaviour of the fibers, respectively.

Background

Over the past few decades, there has been a rising desire for new structural aerospace materials with light-weight, high modulus and high thermal stability that has motivated the advance of materials science. Non-oxide ceramic matrix composites (CMCs) are known to fulfill all the demands because of the low density, remarkable mechanical strength and chemical resistance as well as elevated fracture toughness by fiber-reinforcement. The microporous and micro-cracked matrix allows several times higher strain-to-failure than monolithic ceramics that makes it one of the optimum structural materials at high temperature¹²¹, while reinforcement contribution is mainly toward properties such as electrical conductivity, hardness, thermal expansion and shock resistance.

Polymer-Derived Ceramic Fibers (PDCFs) are considered an admirable reinforcement for CMCs due to improved properties and ease of fabrication by the recent innovations in polymer fiber fabrication technique¹²². Over last three decades, silicon-based advanced ceramics with a variety of desirable properties, such as remarkable chemical resistance, thermal stability and mechanical strength, have been designed with the help of straightforward polymer-to-ceramic conversion^{123;124}. The mechanical properties of PDCFs have been reported as high as 2.5 GPa in tensile strength with 300 GPa in modulus with thermal stability up to 2200 °C¹²⁵.

With the rising demand for better processability, higher ceramic yield and enhanced properties of final ceramic product, numbers of new silicon based preceramic polymers were synthesized in the 1980s with modified properties that is sufficient enough for spinning^{126–129}. The large-scale production of ceramic fibers started early as 1990s³. Either melt- or dry-spinning was applied to mainly polysilanes or polyborosilazanes to produce non-oxide SiC or SiBCN fibers. In terms of melt-spinning, modified polymer with required viscosity is

continuously fed through a heated (about 150 °C) nozzle with hundreds of holes. Fibers are effectively drawn in this way and cured by additional thermal or chemical treatments³. Up until recently, there are many types of ceramic fibers developed over 20 years ago and still commercially available from various manufacturers, such as Hi-Nicalon (from COI), Sylramic (from UBE), etc.

Currently, both oxide or non-oxide (from polymer pyrolysis route) ceramic fibers are widely applied for high temperature applications. Oxide fibers usually delivers higher oxidation resistance compared to non-oxide fibers, while better creep resistance and strength retention allow non-oxide fibers to be even more suitable for ultrahigh temperature applications, such as aerospace components. However, polycarbosilane, main precursor of SiC fibers, is still costly and limited in availability. Hence, ceramic fibers with extremely lower cost and slightly compromised properties are of great interest^{12;22;23}. Recently, other Si-based ceramics by PDC routes, such as the ternary silicon carbonitride SiCN¹³⁰. The formation of SiO₂ and Si₂N₂O double layered structure generates increased diffusion barrier, thus to enhanced oxidation resistance^{131;132}. Consequently, preceramic polymers with higher N content may yield PDCs with improved thermal and oxidation stability of the final ceramic product.

Here, we report a new approach to synthesize carbon-rich SiOCN ceramic fibers via hand drawing and pyrolysis of a cyclic-silazane/polyacrylic acid (PAA) hybrid polymer. The hybrid approach involving hand spinning process is highly efficient for lab scale testing and to develop fundamental understanding related to processing of preceramic fibers and related polymer to ceramic transformations without the need for complex fiber drawing equipment. 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl-cyclotetrasilazane (referred as TTCSZ hereafter) is an organosilazane, whose properties have not been reported when compared to its siloxane analogue, 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl-cyclotetrasiloxane. Although, this type of silazane is crosslinkable at elevated temperature, but it is not known to form fibers in its neat form. Hence, PAA is introduced to improve the spinnability of pre-ceramic polymer. As-prepared fibers were firstly crosslinked at lower temperature in open air, then pyrolyzed at higher temperature for polymer-to-ceramic conversion under the protection of argon. Synthesis, characterization, pyrolysis and phase formation are discussed in detail for

TTCSZ/PAA hybrid fibers in the following sections.

4.1 Experimental

4.1.1 Materials

All the syntheses were conducted with as-received materials without further treatment or purification. The TTCSZ is available from Gelest (USA). The polyacrylic acid (PAA) is purchased from Sigma-Aldrich (USA). Dicumyl peroxide (DCP) as crosslinking initiator is obtained from Sigma-Aldrich (USA). The fiber drawing, handling and crosslinking processes are performed in open air, except pyrolysis which is carried out in ultrahigh purity argon atmosphere from Matheson (USA).

4.1.2 Fiber drawing and pyrolysis

TTCSZ/PAA hybrid fibers were prepared via sol-gel process (Fig. 1). 10 wt % of DCP initially dissolved in TTCSZ formed a solution. PAA was initially mixed with deionized water (PAA to di-water wt ratio 4:1) and stirred until the mixture turned completely into transparent gel. TTCSZ solution was then added to the gel (TTCSZ solution to PAA wt ratio 1:1). After complete mixing by stirring, the PAA/TTCSZ/water system formed a piece of white slurry with a viscosity measured to be about 250 P (Poise) or 25 Pa.s. The overall ratio between TTCSZ: DCP: PAA was 45: 5: 50 wt %. The fiber drawing process is carried out by hand drawing in open air. The hybrid fibers can be conveniently drawn directly from the slurry using metal rods, spatulas or tweezers onto aluminum boats for crosslinking process. Then the fibers are dried and crosslinked in a low temperature oven at 160 °C for 24 hours in air. The aluminum boats are simply hand crafted with aluminum foils which have several advantages to be applied in this process. The aluminum foil is chemically and mechanically stable as a supporter that does not introduce extra impurities in low temperature open-air environment; the shrinkage of the hybrid fibers during crosslinking process can be well controlled by the boat; the scale of the boat can be determined by the size of the oven.

Fibers are collected from aluminum boat after crosslinking, then relocated and wrapped on a small boat or rod support made with ceramics or quartz for high temperature pyrolysis.

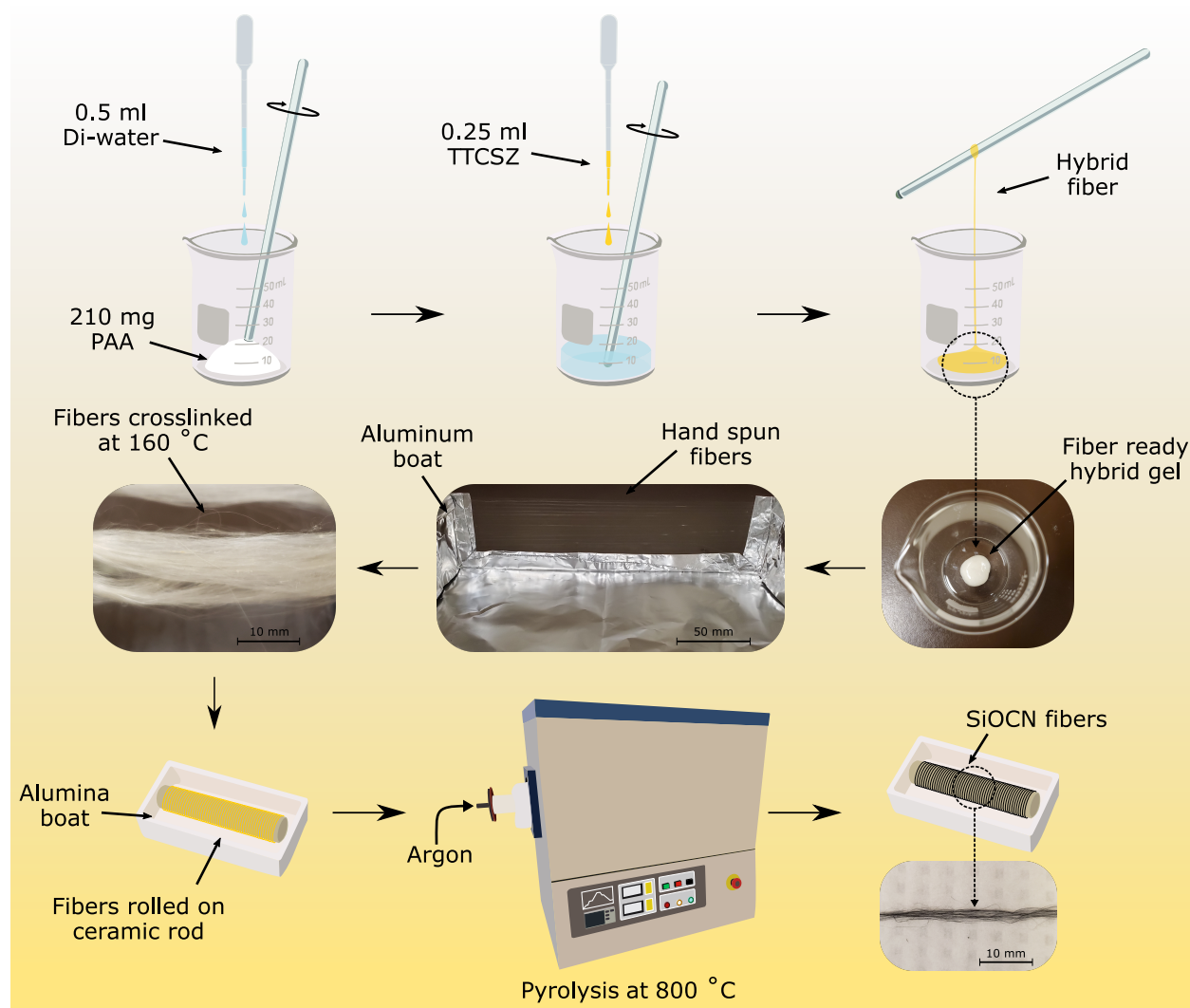


Figure 4.1: *Schematics of fiber drawing process via hand spinning.*

The polymer-to-ceramic transformation is performed at three different temperatures (600, 700 and 800 °C). The fibers on support are mounted on another alumina boat and heated from room temperature to target temperature at heating rate of 2 °C min⁻¹ in argon.

4.1.3 Characterization

Surface morphology of the fibers at each stage was investigated by scanning electron microscopy (EVO MA10, ZEISS, Germany).

Raman spectroscopy was collected from LabRAM ARAMIS Raman spectrometer (LabRAM HORIBA Jobin Yvon, USA) using a HeNe laser (633 nm) as an excitation source.

Fourier-transform infrared spectroscopy (FT-IR) spectra was obtained from Spectrum 400 FT-IR spectrometer (Perkin Elmer, Waltham, MA) on a diamond crystal top plate of an ATR accessory (GladiATR, Pike Technologies, USA).

Viscosity measurement was performed on Brookfield DV-II+Pro viscometer (Brookfield Engineering, USA) using CEP-40 and CEP-52 cone for neat TTCSZ and TTCSZ/PAA, respectively. 0.5 mL slurry was used with 25 - 200 rpm rotation rate at 37 °C for the measurement.

X-ray photoelectron spectroscopy (XPS) was performed by PHI Quantera SXM (ULVAC-PHI, Japan). Depth-profiling was applied for 15 mins via Ar ion-beam.

Solid-state ^{13}C MAS, CP MAS, and ^{29}Si MAS NMR spectra were recorded on a Bruker AVANCE 300 spectrometer ($B_0 = 7.0\text{ T}$, $\nu_0(^1\text{H}) = 300.29\text{ MHz}$, $\nu_0(^{13}\text{C}) = 75.51\text{ MHz}$, $\nu_0(^{29}\text{Si}) = 59.66\text{ MHz}$) using either 4 mm or 7 mm Bruker probes and spinning frequencies of 10 or 5 kHz. ^{13}C CP MAS experiments were recorded with ramped-amplitude cross-polarization in the ^1H channel to transfer magnetization from ^1H to ^{13}C . (Recycle delay = 3 s, CP contact time = 1 ms, optimized ^1H spin-64 decoupling). Single pulse ^{13}C and ^{29}Si NMR MAS spectra were recorded with recycle delays of 30 and 60 s respectively. Chemical shift values were referenced to TTCSZ for ^{13}C and ^{29}Si .

The fiber thermal resistance was analyzed using thermal gravimetric analysis (TGA). The analysis was performed with TG 209 F1 Libra (NETZSCH, Germany) from 100 to 1000 °C (with heating rate of 10 °C min $^{-1}$) in either N_2 or synthetic air (with flow of 10 mL min $^{-1}$) for crosslinked, pyrolyzed TTCSZ/PAA and neat PAA samples.

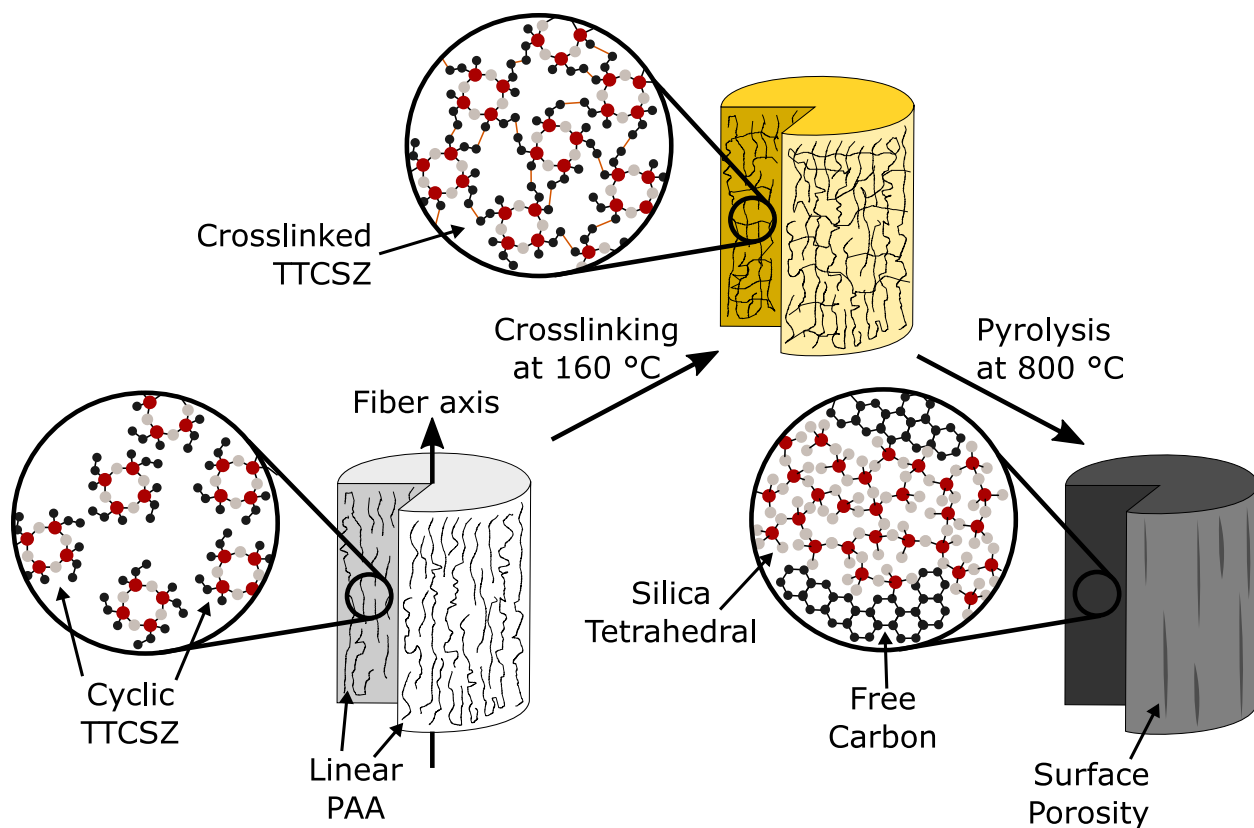


Figure 4.2: Schematics of fiber crosslinking and pyrolysis process. TTCSZ is the main PDC fiber precursor where PAA plays a fiber template role in the hybrid system. TTCSZ molecules are embedded in PAA rigid environment that can be crosslinked at elevated temperature. Within the fibers, PDC nano-domain structures are formed after pyrolyzed at even higher temperature.

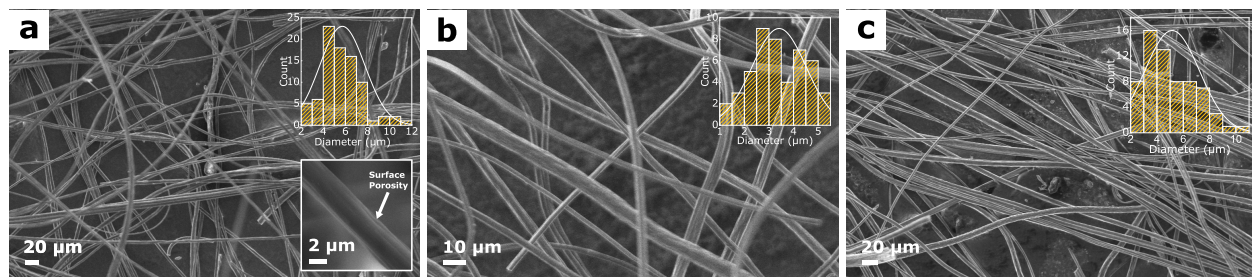


Figure 4.3: SEM images of hand spun TTCSZ/PAA hybrid fibers pyrolyzed at a) 600 °C, b) 700 °C and c) 800 °C. Fibers have diameter distribution of 1 ~ 10 μm with an average diameter about 5 μm. When magnified, fiber surface porosity is noticeable.

4.2 Results and discussion

4.2.1 Characterization of the hybrid fibers

A series of characterization was carried out to determine the properties of as pyrolyzed hybrid PDC fibers. SEM images of the pyrolyzed hybrid fibers are given in Fig. 3 a-c. It is confirmed by SEM that hand-spun fibers have a diameter range of $1 \sim 10 \mu\text{m}$. Each pyrolyzed fibers are considerably uniform in diameter and porous at the surface.

Table 4.1: *Chemical composition of fibers by XPS depth-profiling survey scan in atomic percentage*

Pyrolysis Temperature ($^{\circ}\text{C}$)	Element atomic percentage (at. %)			
	C	Si	O	N
700	71.2	8.6	19.4	0.3
800	50.8	15.5	33.4	0.4

The chemical composition of PDC hybrid fibers are determined by XPS depth-profiling survey scans and the results are listed in Table 1. The presence of oxygen and loss of nitrogen are discussed in the following sections. The existence of “free carbon” was confirmed by Raman spectroscopy. Carbon G-band ($\sim 1595 \text{ cm}^{-1}$) (Fig. 4 d-e) shows the existence of graphitic sp^2 carbon structure in the fibers, while D-band ($\sim 1340 \text{ cm}^{-1}$) represents a large amount of disordered carbon⁴⁸. Specifically, D4- and D3-bands indicate the existence of sp^2 - sp^3 bonds and amorphous carbon in the fibers^{48;133}. Carbon peaks are relatively weaker (high fluorescence) for the fibers pyrolyzed at 600°C indicating less free carbon. For the higher pyrolysis temperature, free carbon amount is significantly increased. Correspondingly, graphitic carbon is increased with the increase of pyrolysis temperature, while the amount of amorphous carbon is decreased. Because Si-C bonds are sp^3 , stronger D1, D4-bands in 700 sample confirms higher SiO_2C_2 and SiO_3C composition discussed below with the NMR analysis (Fig. 5a)¹³⁴. Raman spectra of neat TTCSZ samples are also obtained to find out the contribution of PAA to the pyrolyzed fibers (Fig. 4 b). The free carbon amounts are apparently raised with incorporation of PAA at initial stage by comparing the intensity of the carbon peaks. Further analysis was performed on bonding types and

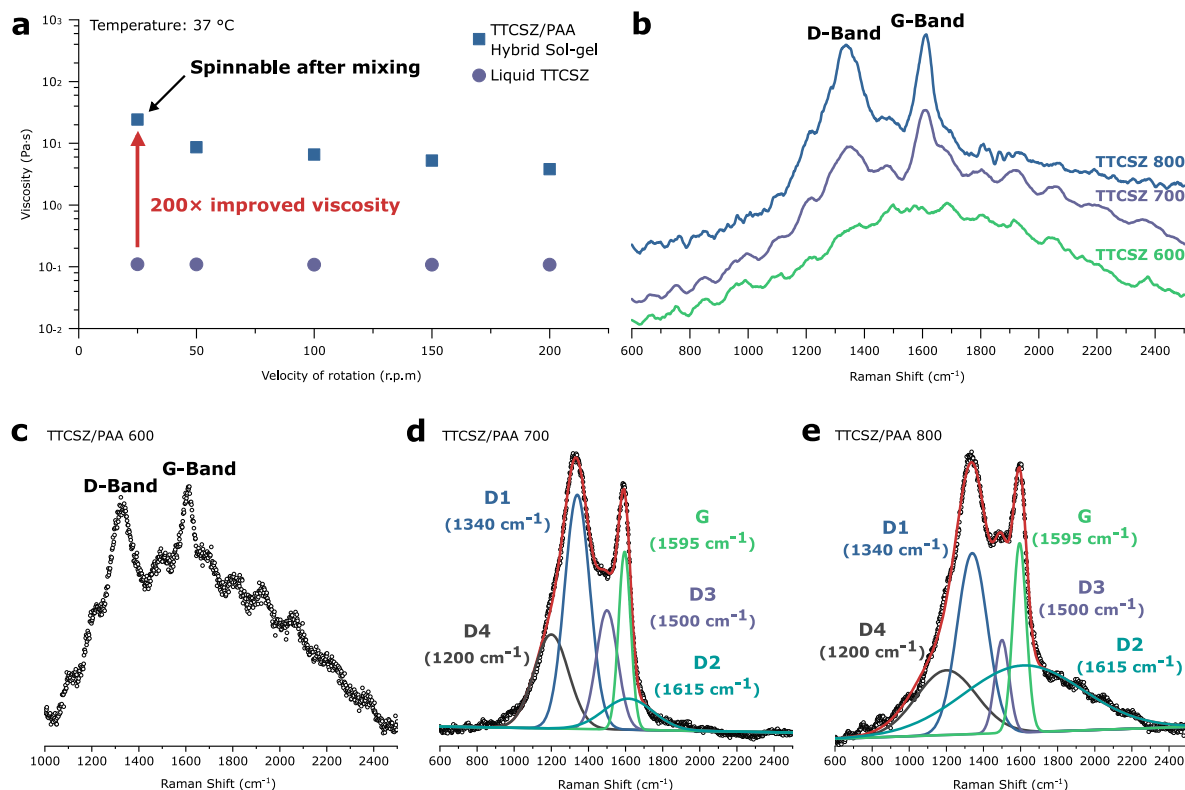


Figure 4.4: a) Viscosity of TTCSZ/PAA slurry and liquid TTCSZ. 200 times improved viscosity is observed after mixing with PAA which enhanced spinnability. b) Raman spectroscopy of TTCSZ pyrolyzed at different temperatures. TTCSZ/PAA hybrid fibers pyrolyzed at c) 600 °C, d) 700 °C and e) 800 °C. Free carbon amount is increased as raised pyrolysis temperature.

molecular structures. NMR spectroscopy investigation was performed on the samples at each pyrolysis temperature (Fig. 5). ^{29}Si MAS NMR spectrum (Fig. 5 a) of the sample heat-treated at 600°C shows components at ~ -20 ppm, ~ -65 ppm and ~ -110 ppm suggesting tetrahedrally coordinated Si in SiO_2C_2 , SiO_3C and SiO_4 species typical of mixed silicon oxycarbide units^{135;136}. It should be noticed that part of the signal at ~ -10 ppm could also correspond to SiN_2C_2 environments¹³⁷ but probably in small proportions. This point will be further discussed in part 3.3. The strong intensity of SiO_3C signal indicates a significant amount of C bonded to Si atoms and correspondingly less free carbon, this result well matches with the Raman data. When increasing the pyrolysis temperatures, the fractions of mixed silicon oxycarbide units decreases: SiO_3C peak greatly decreases and

SiO_2C_2 peak disappears completely. SiO_3C peak further decreases at 800 °C and leaving most of Si atoms in silica tetrahedral form.

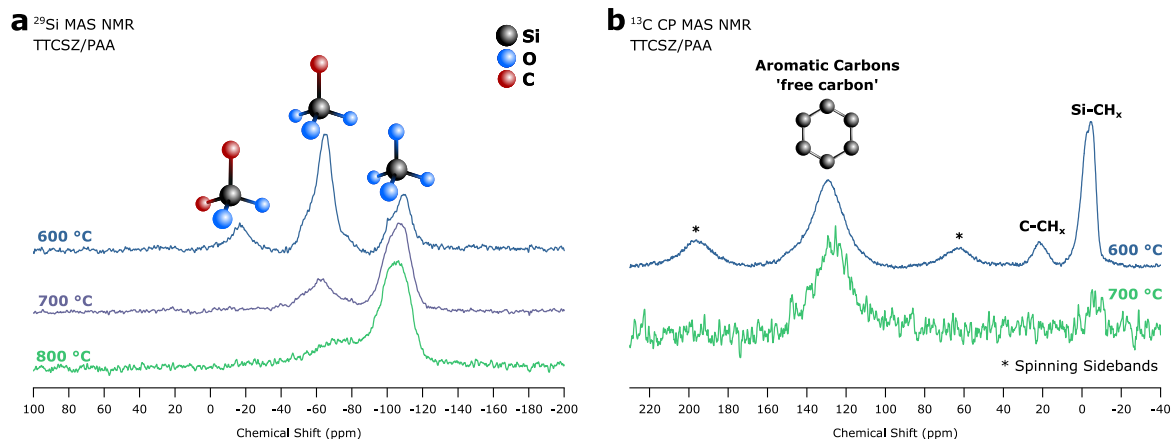


Figure 4.5: Solid-state NMR spectra of pyrolyzed TTCSZ/PAA hybrid fibers at 600, 700 and 800 °C (a) ^{29}Si MAS (b) ^{13}C CP MAS with corresponding micro structure shown. A significant drop in Si-C bonds is noticed as increasing of pyrolysis temperature. Number of scans (NS): ^{29}Si MAS 600 °C (NS = 1334), 700 °C (NS = 1122), 800 °C (NS = 4186); ^{13}C CP MAS 600 °C (NS = 2400), 700 °C (NS = 2784).

^{13}C CP MAS NMR results (Fig. 5 b) show a clear free carbon peak around 130 ppm for both 600 and 700 °C. No remaining vinyl groups are observed after pyrolysis suggesting a complete polymerization into aliphatic carbons while a strong Si-C peak is detected at 600 °C which drastically decreases at 700 °C.

Further NMR spectra were recorded from TTCSZ/PAA hybrid fibers and neat TTCSZ powders samples pyrolyzed at 700 °C (Fig. 6) to investigate the effect of PAA on the structure of the final product. From the comparison, neat TTCSZ at 700 °C shows a spectrum very close to TTCSZ/PAA at 600 °C. As it has been already shown in Raman analysis, either incorporation of PAA or rising in pyrolysis temperature will ultimately result in a structure with elevated “free carbon” content and decreased Si-C bonds. This is also confirmed by ^{13}C CP MAS NMR data showing increased “free carbon” content and decreased Si-CH_x signals in TTCSZ/PAA hybrid sample compared to neat TTCSZ.

XPS analysis was applied to determine the bonding type (Fig. 7) from survey scan and high-resolution scan of O1s, C1s, Si2s, Si2p and N1s peaks in each samples¹⁰⁴. From

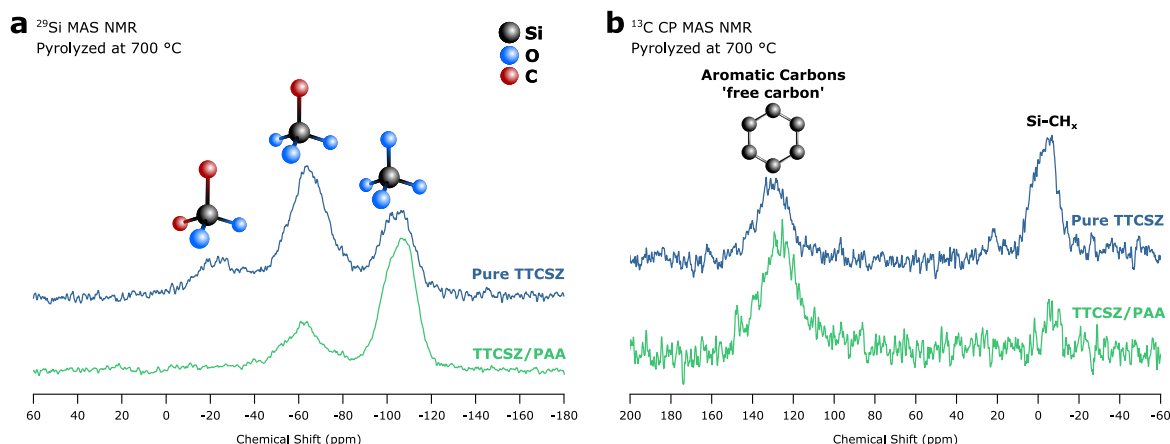


Figure 4.6: Solid-state NMR spectra of TTCSZ/PAA fibers and neat TTCSZ at 700 °C (a) ^{29}Si MAS (b) ^{13}C CP MAS. Under the same pyrolysis temperature, incorporation of PAA leads to increased free carbon and decreased Si-C bonds. Number of scans (NS): ^{29}Si MAS neat TTCSZ (NS = 1396), TTCSZ/PAA (NS = 1122); ^{13}C CP MAS neat TTCSZ (NS = 2736), TTCSZ/PAA (NS = 2784).

the survey scan, N1s peak disappears after pyrolysis above 600 °C. High resolution scans of major peaks reveals the merging of different signals, such as Si-C peaks at ~ 102.0 eV in Si2p scan and ~ 284.6 eV in C1s scan¹⁰⁴. SiO_2C_2 , SiO_3C and SiO_4 components can be obtained from hybrid fibers pyrolyzed at 600 °C in agreement with the NMR results¹¹⁸. From high-resolution C1s scan (Fig. 7 a.3, b.3, c.3), the C-Si component is continuously decreased leading to relative increase in C-C as pyrolysis temperature increases. This result also matches the FT-IR spectra in Fig 8.

4.2.2 Spinnability

Initial attempts were made to draw fibers directly from neat liquid TTCSZ. The rapid crosslinking was observed at about 125 °C with 10 wt % crosslinking initiator DCP and completely transformed TTCSZ liquid into a hard bulk, without an intermediate viscous status that can initiate spinning process. The failure was due to two main reason: low viscosity (Fig. 4 a) and cyclic structure of TTCSZ. PAA was introduced to the initial fiber drawing stage before crosslinking to improve spinnability of TTCSZ. Viscosity measurement showed low viscosity (~ 0.1 Pa s at 37 °C) for liquid TTCSZ with 10 wt% DCP. After mixing

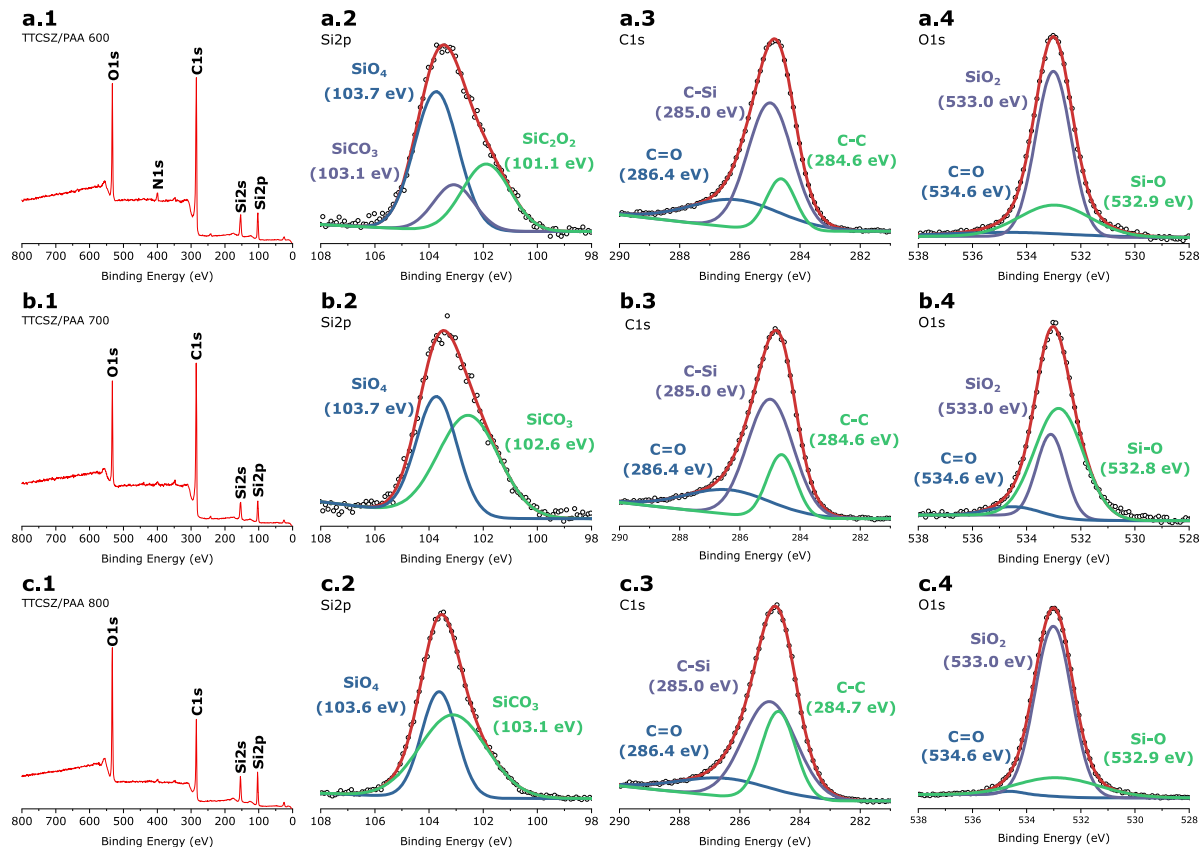


Figure 4.7: XPS results of PDC fibers from TTCSZ/PAA hybrid precursor. a-c.1) Survey scan. High resolution scan of Si2p, C1s and O1s of samples pyrolyzed at a.2-4) 600 °C, b.2-4) 700 °C and c.2-4) 800 °C. From a.3 to c.3, there is a huge increase in C-C/C-Si ratio.

with PAA, viscosity was raised more than 200 times to about 25 Pa s at shear rate of 25 rpm (or 50 cm s^{-1}) which met the requirement for sol-gel spinning ($> 10 \text{ P}$)¹³⁸. Besides, ^{13}C CP MAS NMR (Fig. 9) shows broad signals (suggesting low mobility) of $-\text{CH}(\text{COOH})-\text{CH}_2-$ species which is responsible for enhanced spinnability.

4.2.3 Crosslinking and pyrolysis behavior

Investigation of crosslinking behavior is essential since the final content of PDC fibers is largely determined by the bonds formed during crosslinking stage. FT-IR analysis were obtained with main bands characteristics of raw PAA fibers^{139–141}, neat PAA fibers heated at 160 °C, and TTCSZ/PAA hybrid raw, crosslinked and pyrolyzed fibers^{142;143}. The weak

influence of DCP on FT-IR signal is discussed in supplemental material (Fig. S1). FT-IR is mainly used to investigate the crosslinking behavior of the precursors¹⁴². The changes between the precursor spectra and the crosslinked spectra reveal a critical loss of hydrogen and nitrogen during crosslinking. The excessive oxygen content is possibly imported by the initiator, adsorbed from the air or introduced during reaction with water (discussed below). Moreover, the majority of organic moieties (methyl and vinyl groups) are eliminated during this process along with the crosslinking evidence shown in the Fig. 8 a.

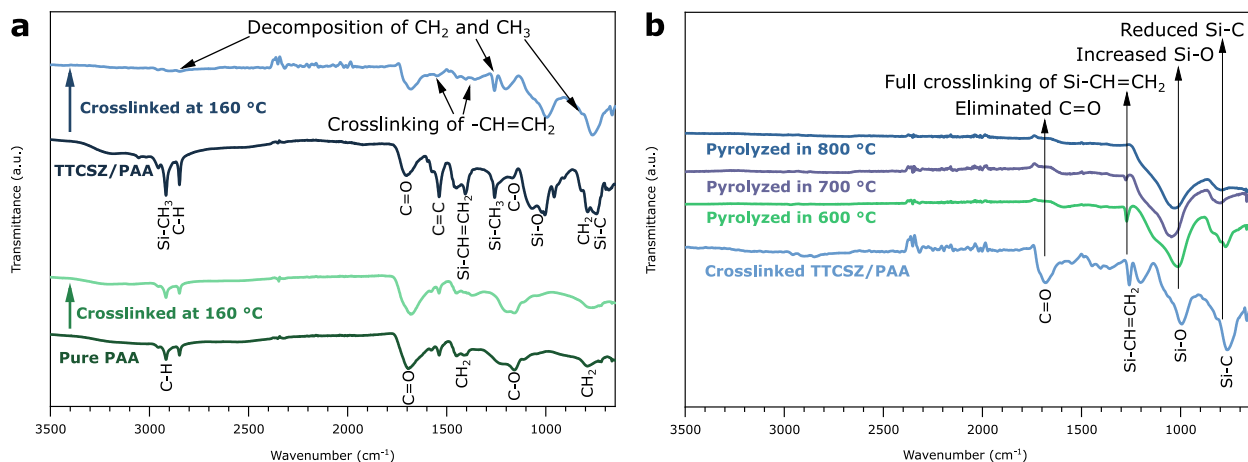


Figure 4.8: FT-IR spectra of TTCSZ/PAA hybrid fibers a) crosslinked at 160 °C, b) pyrolyzed at 600, 700 and 800 °C. At crosslinking stage, decomposition of CH_2 and CH_3 , crosslinking of $-\text{CH}=\text{CH}_2$ are clearly observed.

In order to investigate the effect of DCP on FTIR signals, we performed additional FTIR analysis (results shown in Figure 2.9) on neat dicumyl peroxide (DCP), TTCSZ + DCP (10 wt. %) mixture and crosslinked TTCSZ + DCP (10 %). DCP is not detectable from the FTIR of TTCSZ+DCP mixture (the signature peaks are extremely weak). Especially after crosslinking at 160 °C, DCP signal became completely undetectable by FTIR. Hence, it is fair to assume that the DCP is washed away or decomposed at the crosslinking stage.

We performed FTIR on TTCSZ (10 wt % DCP) and crosslinked TTCSZ (10 wt % DCP), shown in Figure 2.10. When comparing this result with previous FTIR data, several points can be made: (1) Neat PAA and PAA heated at 160 °C did not show significant changes in FTIR spectrum. (2) Comparing TTCSZ/PAA crosslinked at 160 °C and TTCSZ crosslinked at 160 °C without the PAA, the main differences lie at the PAA peaks ($\text{C}=\text{O}$, CH_2 and $\text{C}-\text{O}$

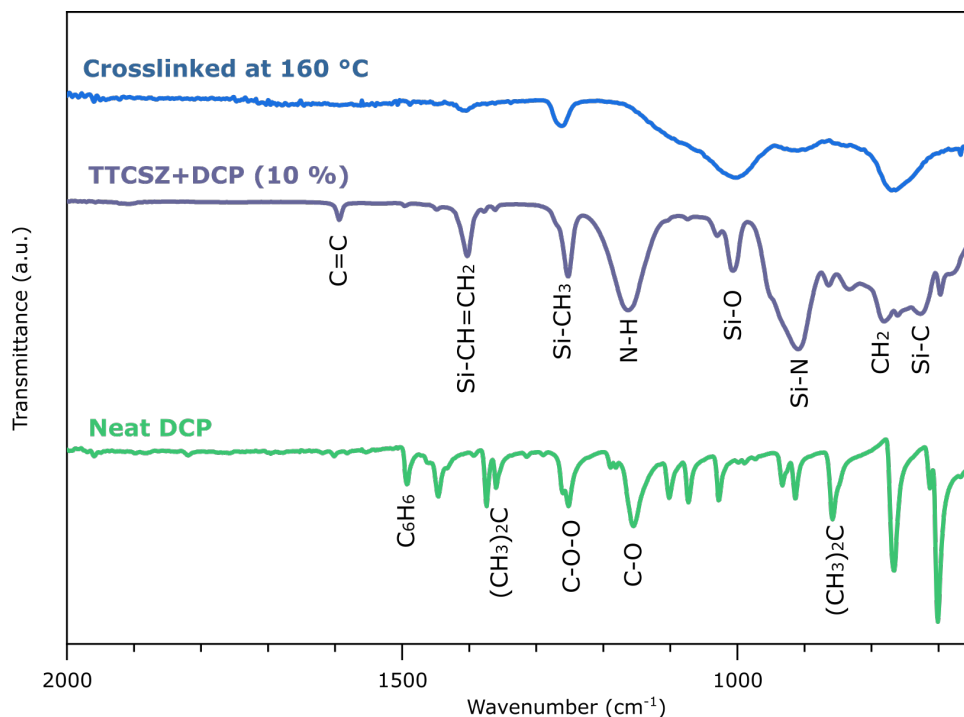


Figure 4.9: Influence of DCP on FTIR signal. The FTIR spectra of neat DCP, TTCSZ+DCP (10 wt. %) and TTCSZ+DCP (10 wt. %) crosslinked at 160 °C are presented.

peak, circled in the figure). Based on the abovementioned points, introduction of PAA in to TTCSZ had little or no effect on the chemical structure of TTCSZ. Hence, it is fair to conclude that no chemical reaction took place between PAA and TTCSZ during the physical mixing at room temperature or during heating at 160 °C.

NMR on raw and crosslinked samples supports FT-IR results in Figure 2.11. Both ^{13}C MAS and ^{13}C CP MAS NMR were obtained for raw fibers to determine, respectively, highly mobile components (TTCSZ) and rigid environments (PAA). Before crosslinking, both ^{29}Si and ^{13}C MAS spectra show narrow signals indicating high mobility species: ^{29}Si peaks are mainly observed around -35 ppm, a position significantly different from the initial TTCSZ+DCP solution showing signals at -14.7 ppm and -17.5 ppm (Figure 2.11a inset) characteristic of 6-ring 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane¹⁴⁴ and 8-rings silazane TTCSZ respectively. Signals around -33 ppm are indeed reported for 1,3,5,7-tetravinyl-1,3,5,7-tetracyclotetrasiloxane¹⁴⁵. This strongly suggests a significant oxidation of the silazane rings into siloxanes, possibly due to the addition of water with PAA. Nonetheless, additional

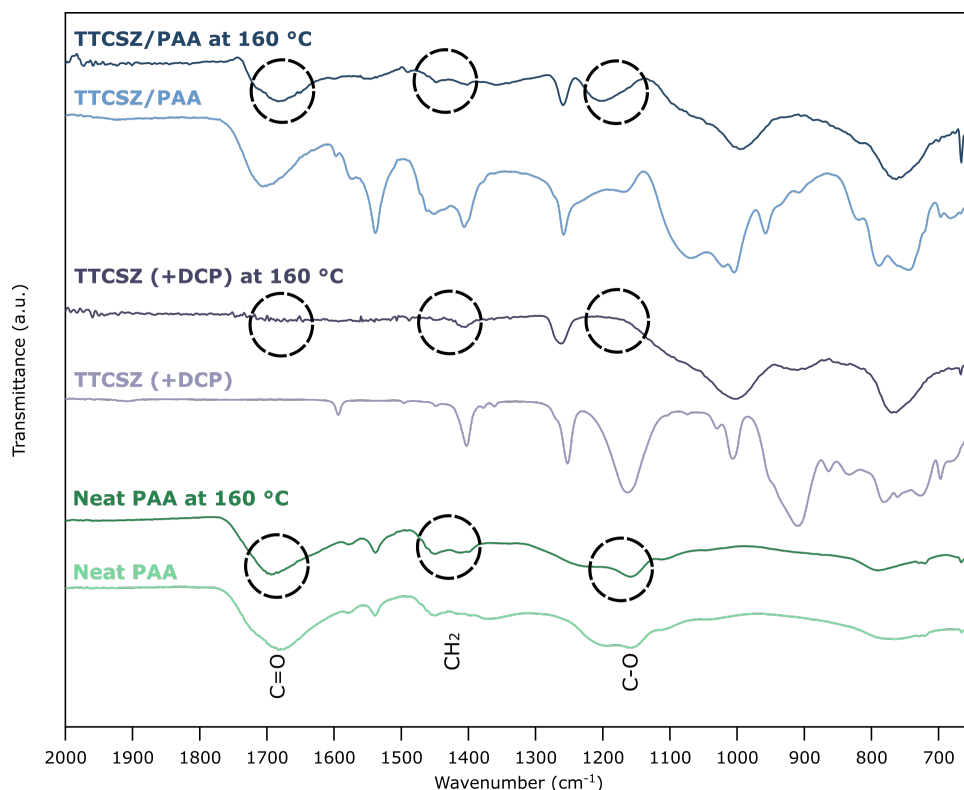
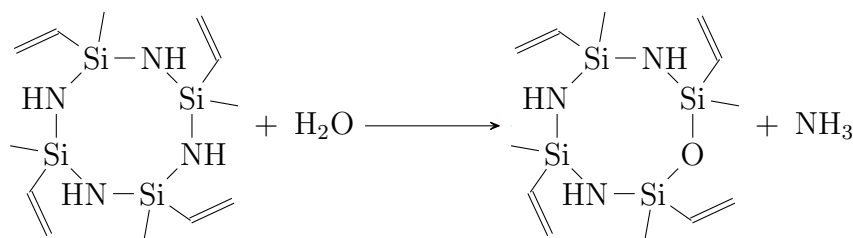


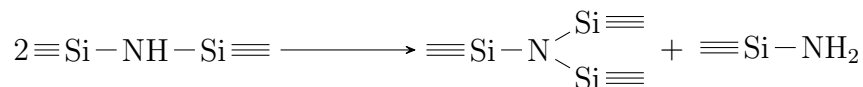
Figure 4.10: Weak or no crosslinking between PAA and TTCSZ. FTIR spectra of neat PAA, TTCSZ (DCP 10 wt. %) and TTCSZ/PAA and corresponding heat treated samples.

minor signals are still present around -17 ppm, indicating that silazane bonds are still present.

At this point, from the strong evidence obtained from NMR analysis, two different hypotheses are proposed here to explain the loss of nitrogen before pyrolysis: (1) A large amount of the nitrogen loss may be addressed to the pre-spinning mixing stage. $-NH-$ may react with H_2O molecules and form NH_3 inducing nitrogen loss before crosslinking.



(2) During crosslinking stage, the hydrosilylation reaction takes place. This reaction is induced by heating and happens at relative lower temperature as low as 120°C ^{146;147}.



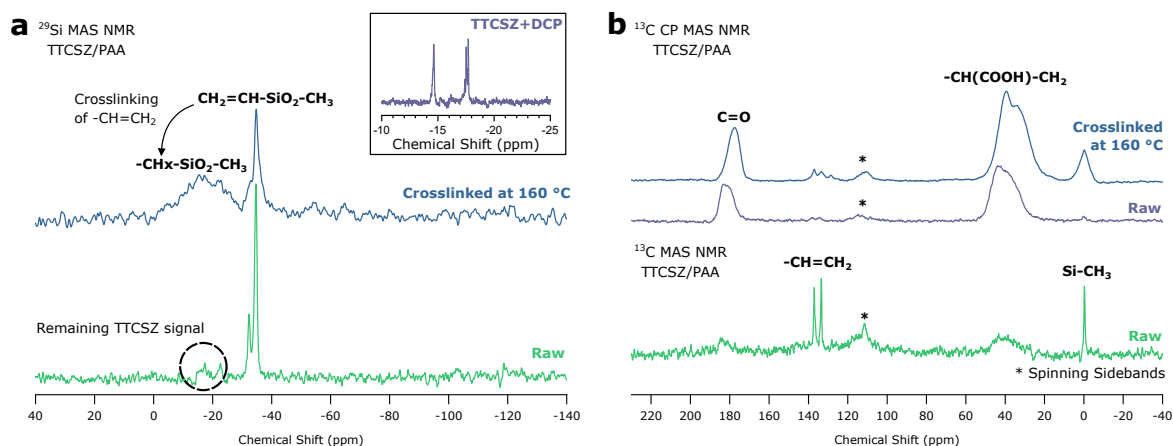
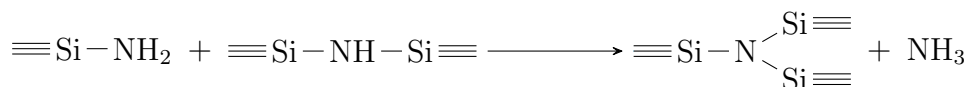
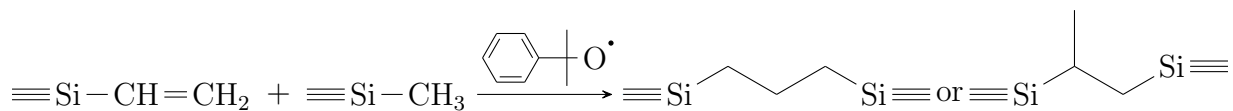


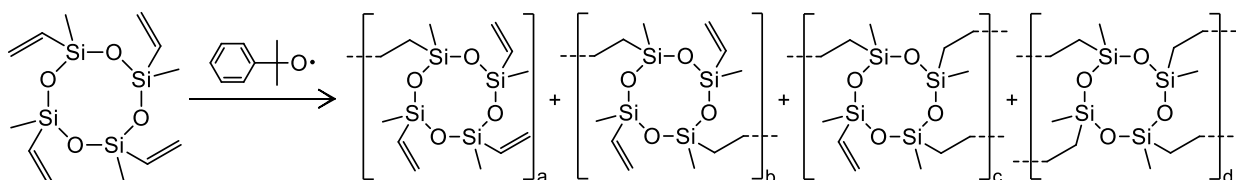
Figure 4.11: Solid-state NMR spectra of TTCSZ/PAA hybrid raw fibers and crosslinked fibers. ^{29}Si MAS NMR result indicates decreased mobility after crosslinking, and ^{13}C showed very low interaction between PAA (rigid environment) and TTCSZ at crosslinking stage. Number of scans (NS): ^{29}Si MAS Crosslinked at 160 °C (NS = 474), Raw (NS = 140); ^{13}C CP MAS Crosslinked at 160 °C (NS = 1056), Raw (NS = 432); ^{13}C MAS Raw (NS = 56).



As a result, TTCSZ may be oxidized to 1, 3, 5, 7-tetramethyl-1, 3, 5, 7-tetravinylcyclotetrasiloxane. Then methyl-vinyl radical reaction will take place initiated by DCP during crosslinking stage. The reaction can be shown as follow¹⁴⁸.



And the reactions are expected to take place on all four vinyl groups attached to four cyclic silicon atoms and form into network structure. However, this crosslinking reaction may not be complete due to the limited mobility after the network formation^{147;148}.



After crosslinking at 160 °C, broader peaks indicate less mobility due to the conversion of Vi-(Me)SiO₂ to -CH₂-(Me)SiO₂. However, high consistency between raw and 160 °C

^{13}C CP MAS suggests very weak PAA crosslinking activities at 160 °C. Further discussion regarding crosslinking behavior between PAA and TTCSZ is presented in supplemental material (Fig. S2).

Polymer-to-ceramic conversion process is revealed at 600 °C which is supported by Raman analysis showing free carbon bands in Fig. 3. However, Comparison of FTIR results between crosslinked fibers and pyrolyzed fibers suggests that the conversion is not complete until 800 °C. The decomposition of remaining organic groups is observed at pyrolysis temperature range (600 - 800 °C).

4.2.4 Thermal resistance

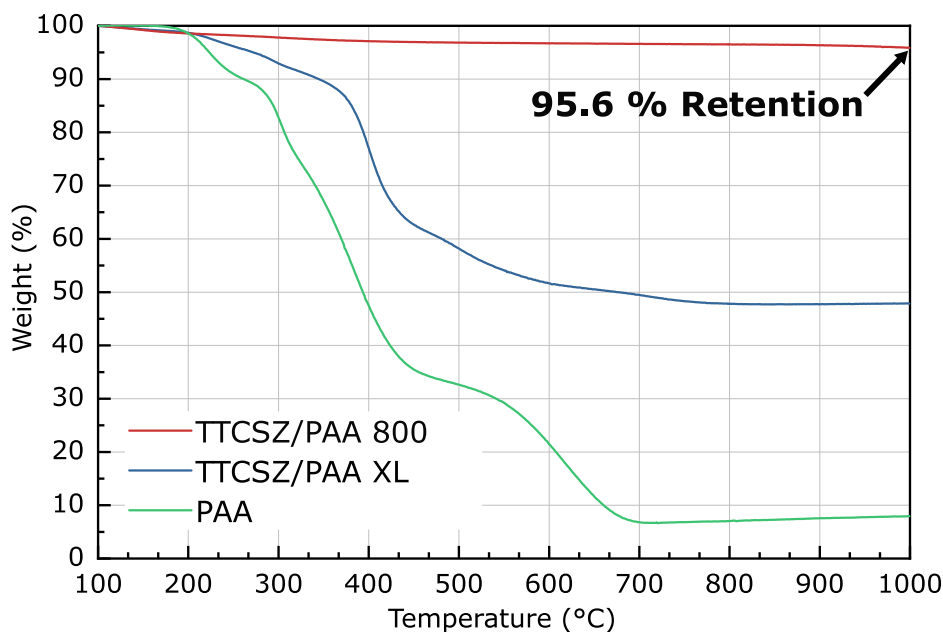


Figure 4.12: TGA analysis of TTCSZ/PAA hybrid pyrolyzed at 800 °C and weight change recorded in N_2 ; TTCSZ/PAA hybrid crosslinked at 160 °C and weight change recorded in N_2 ; neat PAA sample and weight change recorded in air.

The thermal behavior of the hybrid fibers is studied with thermogravimetric analysis using powder samples in either N_2 or air and the results are shown in (Fig. 10). The significant weight loss of neat PAA fibers started at a temperature as low as 200 °C. The

hybrid fibers pyrolyzed at 800 °C showed a good thermal stability up to 1000 °C with weight loss of 4.5 wt. %. While the TGA curve of crosslinked hybrid samples gives a rough idea of ceramic yield of this TTCSZ/PAA combination. The estimated yield in of crosslinked sample is about 48 % according to (Fig. 10) which well matches with the recorded ceramic yield. TGA result of neat PAA in air, associated with NMR results, indicates that PAA in the hybrid system mainly acts as a fiber template (rigid environment mentioned above) in the spinning process and does not participate in crosslinking (^{13}C CP MAS NMR), and provides a small amount of excessive carbon after pyrolysis.

BET analysis

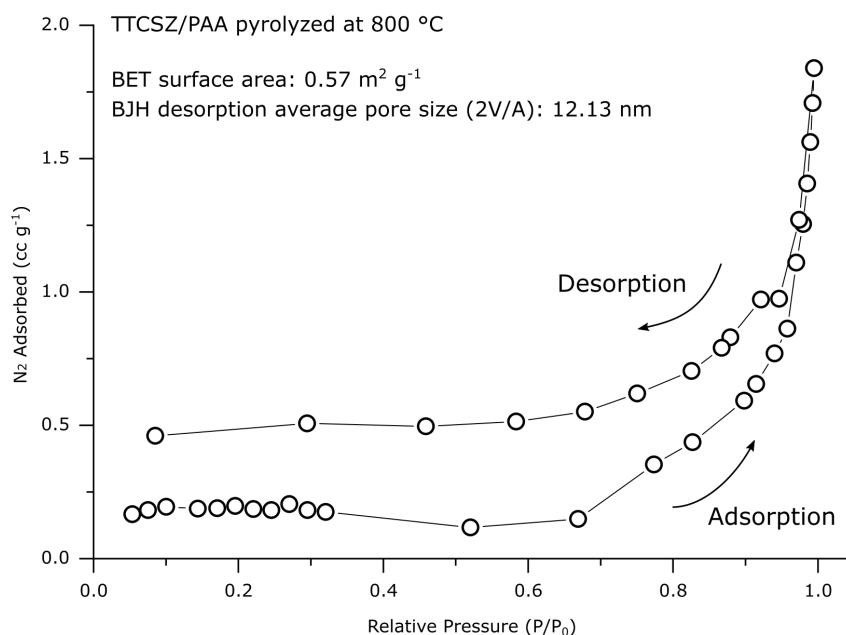


Figure 4.13: BET analysis result on TTCSZ/PAA pyrolyzed at 800 °C. The data plotted shows the N₂ adsorption/desorption isotherm of the fiber samples with BET surface area and average pore size shown.

Additional BET analysis was performed on the pyrolyzed fiber samples using ASAP 2460 Surface Area and Porosimetry Analyzer (Micromeritics) in N₂ at 77.3 K. This adsorption curve resemble to type II isotherm, where most of the gas molecules are adsorbed on non-porous or macroporous surface. The hysteresis of the curves strongly suggest the existences

of pore network structures with macro pores (> 50 nm). The corresponding results are shown in the Fig S3. The BET analysis results show a moderate BET surface area of $0.57 \text{ m}^2 \text{ g}^{-1}$.

4.3 Conclusion

Carbon-rich SiOCN fibers are synthesized and reported in this work, for the first time, from commercially available 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl-cyclotetrasilazane and PAA forming a hybrid preceramic polymer precursor. The sol-gel process, fiber drawing and crosslinking processes are easily conducted in open air. Linear PAA molecules provide rigid body during fiber drawing process and provide excessive free carbon in the final fiber product. As-spun fibers are revealed oxygen rich which may be due to the presence of water during mixing stage, still, providing intrinsic thermal stability at 1000°C .

The fibers products are uniform in diameter even with hand spinning. A small degree of surface porosity (without large defects) observed from the fibers during the characterization (BET surface analysis data presented in the supplemental material Fig. S3). The spinning process and technique developed in this work successfully produced fibers from an unspinnable silazane with acceptable compromise in composition and properties, but greatly reduced processing cost and environmental requirement. This hybrid technique is recommended to lab scale early production of new types of ceramic fibers. High productivity of this technique can easily satisfy various characterization needs with minimum setup requirement. The fiber products are suggested as reinforcement for CMC materials.

The fibers structure and properties may be improved by altering synthesis condition. Oxygen content can be controlled from the initial fiber drawing stage to crosslinking stage: instead of mixing TTCSZ/PAA in aqueous environment, melt-spinning is applicable to avoid the reaction between TTCSZ and water molecule, where this process may be conducted in a glovebox; crosslinking environment may be adjusted to inert atmosphere such as N_2 or Ar to avoid fibers from direct contact with O_2 ; crosslinking method may also be altered to irradiation (gamma or electron), photo (UV) or ionic crosslinking instead of thermal crosslinking.

Chapter 5

Fabrication and Characterization of High Temperature Silicon OxycarbideElectrospun SiOC Fiber-mats via Electrospinning of Polyvinylpyrrolidone/Preceramic Siloxanes Hybrid Systems

Preview

Electrospinning is an emerging technique for synthesizing micron to submicron-sized polymer fiber supports for applications in energy storage, catalysis, filtration, drug delivery and so on. However, fabrication of electrospun ceramic fiber mats for use as a reinforcement phase in ceramic matrix composites or CMC for aerospace applications remains largely unexplored. This is mainly due to stringent operating requirements that require a combination of properties such as low mass density, high strength, and ultrahigh temperature resistance. Herein we

report fabrication of molecular precursor-derived silicon oxycarbide or SiOC fiber mats via electrospinning and pyrolysis of cyclic polysiloxanes-based precursors at significantly lower weight loadings of organic co-spin agent. Ceramic fiber mats, which were free of wrapping, were prepared by a one-step spinning (in air) and post heat-treatment for crosslinking and pyrolysis (in Argon at 800 °C). The pyrolyzed fiber mats were revealed amorphous and few microns in diameter. Four siloxanes-based pre-ceramic polymers were used to study the influence of precursor molecular structure on the compositional and morphological differences of cross-linked and pyrolyzed products. Further mechanical and thermal characterizations suggested the potential of electrospun ceramic mats in high temperature applications.

Background

Silicon-based ceramics have extraordinary potential as high- temperature applications for promising mechanical properties at elevated temperatures and oxidizing environments¹³. Controlled synthesis of one-dimensional non-oxide ceramic fibers, whiskers, or rods has been widely studied^{149;150}. Until the discovery of polymer-derived ceramic (PDC), ceramic fibers were nearly unachievable via powder-based conventional ceramic manufacturing techniques¹⁴⁹. PDC, however, is beneficial for the manufacturing of complex structured ceramic components, such as fibers, films/coatings, or ceramic matrix composites (CMCs), due to its ease of handling, improved processability, decreased processing temperature, and controllable preceramic compositions, which allow the application of a variety of preforming techniques to draw fibers from preceramic dry, wet, melt spinning, and electrospinning polymers¹³.

In our previous work¹⁵¹, we prepared handspun PDC fibers from cyclic silazane using linear polymer (i.e., polyacrylic acid) as a spinning agent. This polymer acted as a template to form the fibers, while the silazane molecules were embedded or gathered on the surface of the fiber template. The silazane molecules then crosslinked and formed a rigid structure, even causing solidification if used pure. After pyrolysis, crosslinked silazanes converted into ceramics and the polyacrylic acid (PAA) decomposed, contributing free carbons to the final product. Although hand spinning produces uniform, long fibers, the high requirement of sol-

gel morphology and extensive amount of human involvement required decrease its efficiency for mass production.

Electrospinning is a flexible, scalable technique that utilizes a simple setup and easy operation to draw micron to sub-micron fibers from molten polymers or polymer solutions^{149;152;153}. Electrospun ultra-thin fibers are desirable for applications such as electronics, photonics, sensing, filter, biomedical, or reinforcement applications^{154;155}. Compared to hand spinning, electrospinning is more efficient with well-controlled fiber diameter distribution. Substantial electrostatic charges, which are caused by the electrical field between the spinning needle and the collector, form the fibers¹⁵⁶. The fiber mats can then be heat treated to ceramic fibers using PDCs¹⁵⁷. The spinning solution is usually made of at least one preceramic precursor and a solvent that evaporates during spinning¹⁵⁷. Additionally, an organic polymer may be added as a spinning agent to optimize viscosity. Fiber diameter is controllable primarily via sol-gel properties (i.e., viscosity, conductivity, and surface tension) and spinning parameters (i.e., electrical potential and distance between the tip and collector)^{154;158;159}. Likewise, fiber morphology is effectively tunable via spinning, crosslinking, and pyrolysis conditions.

A limited amount of research has demonstrated the electrospinning of SiOC^{160–162}, SiOCN^{163–165}, SiCN, or SiBCN¹⁶⁶ fibers via PDCs. These fibers are usually synthesized from a mixture of linear polysiloxane (or polysilazane) and linear organic polymer, such as polyacrylonitrile or polyvinylpyrrolidone (PVP). Most fibers synthesized uniform ceramic fibers with diameters ranging from hundreds of nanometers to several micrometers. Research has also shown further implementations of electrospun fiber mats for aerogel growth¹⁶⁷, nanowire growth^{161;166}, and electrochemical applications^{162;164}. In the previous studies, pyrolyzed ceramic fiber surface and cross-section features were well determined with via high resolution scanning electron microscopy (SEM) or transmission electron microscope (TEM) techniques; chemical compositions were also reported by various analysis. However, characterizations of as-spun raw fiber mats and crosslinked fiber mats were often ignored. As a result, the evolution or development of chemical compositions, bonding situations and surface morphologies over each post processing stage remain incomplete. Herein, we carried out a systematic

characterization of fiber mats from the raw state to crosslinked and pyrolyzed state to investigate: 1) the effect of different preceramic precursor on the final product; 2) the crosslinking efficiency of different catalyst; 3) compositional and structural development of the fiber mats; 4) the change of chemical bonding situation after crosslinking and pyrolysis of the fiber mats; 5) mechanical and thermal stability of synthesized fiber mats.

In this work, we studied the SiOC fibers that were electrospun from cyclic oligomer siloxanes and PVP hybrid precursors for the first time. Fiber mats were prepared by simple one step mixing and spinning process with isopropanol as the only solvent for siloxanes and PVP. This study utilized 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetra-siloxane (referred to as 4-TTCS), Pt- 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane complex (2 % Pt-4-TTCS complex in 4-TTCS, referred to as Pt-TTCS), 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (referred to as 3-TTCS), and 1,3-divinyl-tetramethyldisiloxane (referred to as DTDS) as SiOC precursors. These siloxanes, that have not been reported for fiber drawing purpose, are readily available and inexpensive, thereby decreasing fiber manufacturing costs compared to costly SiC fibers^{11;13}. The electrospinning was carried out with low PAA (spinning reagent) concentration as 20 wt. %. As-spun fiber mats are crosslinked and pyrolyzed in an inert environment (ultra-high purity argon), and prepared fiber mats are free of wrapping and large enough for lab-scale CMC testing. SEM and TEM revealed the fiber morphologies. Crosslinking reactions of preceramic polymers, PVP, and polymer-to-ceramic conversion were studied via Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR).

5.1 Experimental

Materials

Preceramic silicon oligomers were purchased from Gelest (Pennsylvania, USA), PVP (average Mw $\sim 1,300,000 \text{ g mol}^{-1}$) and dicumyl peroxide (DCP) were obtained from Sigma-Aldrich (Missouri, USA), and isopropanol was obtained from Fisher Chemical (Kansas, USA). Math-

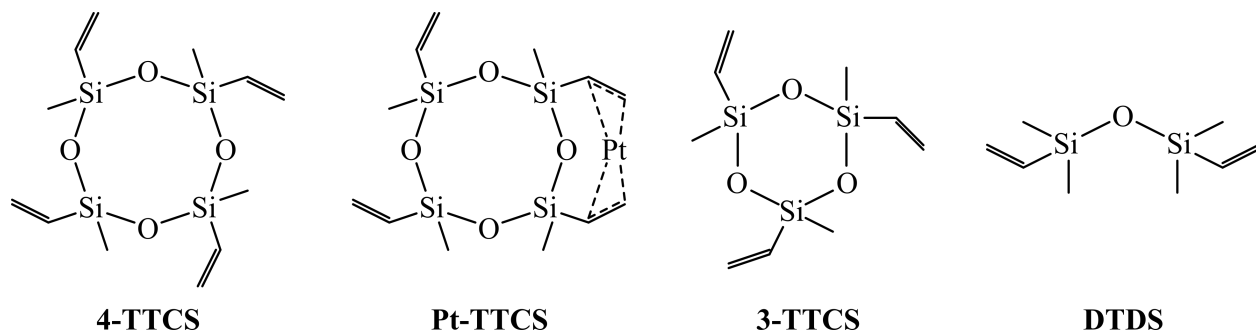
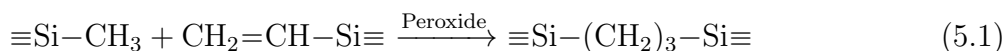


Figure 5.1: *Molecular structure of preceramic silicon oligomers.*

eson (Texas, USA) supplied ultra- high-purity, compressed argon gas to be used as a pyrolysis atmosphere.

Figure 5.1 shows that preceramic silicon oligomers have very similar initial structures to vinyl groups for potential crosslinking spots. Initial compositions differ slightly since 4-TTCS, Pt-TTCS, and 3-TTCS have an overall Si to O ratio of 1:1 and cyclic structures, while the ratio is 2:1 for DTDS. As shown in the following equations, crosslinking by DCP and Pt yields different mechanisms and results:



Electrospinning setup

The electrospinning setup used in this work was designed and assembled within the lab. Figure 5.2 shows the four major parts of the spinning setup: (1) spinning solution feeder made of a syringe mount on a linear slide stroke with a stepper motor; (2) fiber collector as a rotating aluminum cylinder driven by a motor; (3) high-voltage power supply (30 kV maximum); and (4) control system by Arduino, including sensors and motor controller.

Preparation of raw fibers

Siloxanes were initially mixed with 1 % DCP as a crosslinking initiator until DCP was fully dissolved into liquid siloxanes, except for Pt-TTCS, in which Pt acted as the crosslinker.

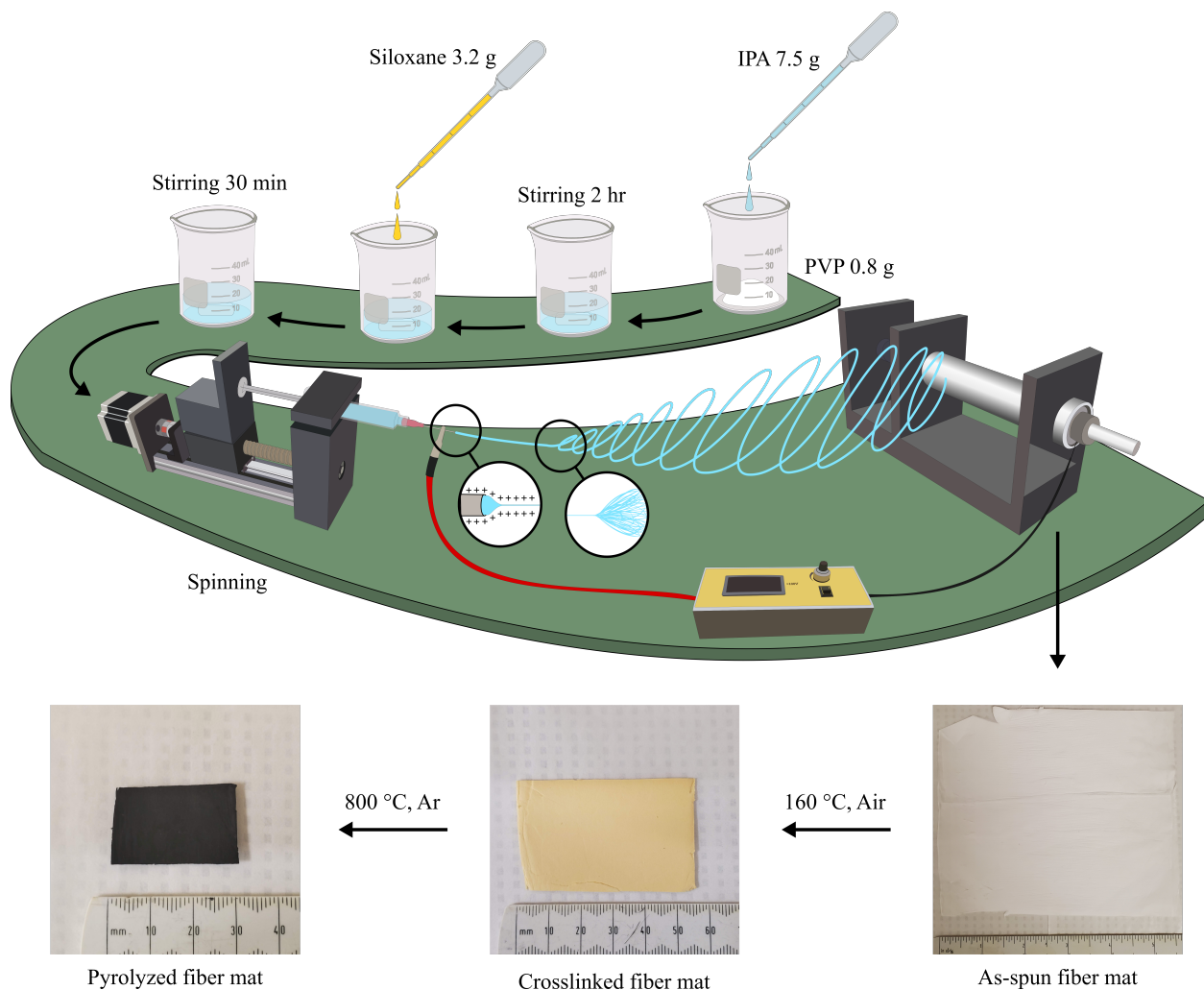


Figure 5.2: *Electrospinning setup.*

In addition, 800 mg of PVP powder was dissolved into isopropanol alcohol (IPA) with the approximate weight ratio of PVP:IPA = 1:9 via magnetic stirring at 300 rpm for 4 hours. Once a uniform solution was formed without visible particles or air bubbles, preceramic siloxanes were added into the solution with extra stirring for 1 hour. The siloxane/PVP hybrid gel was loaded into a 10 ml syringe with a flat metallic needle and fed at the speed of 5 ml hr^{-1} . The needle was subjected to the 15 kV positive output of the high-voltage power supply while the ground was connected to the fiber collector. The distance between the needle tip and the collector was set to 20 cm. A raw fiber mat measuring $\sim 20 \times 20 \text{ cm}^2$ was produced.

Crosslinking and pyrolysis of fiber mats

The as-spun fiber mats were dried in open air for 24 hours and then transferred into the low-temperature oven for crosslinking at 160 °C for 24 hours. Crosslinked mats were cut into small squares to fit into aluminum ceramic boats for pyrolysis, which was performed at a heating rate of 2 °C min⁻¹ and 30 min annealing at the target temperature in the tube furnace with Ar gas (at the flowrate of 5 ml min⁻¹). The target temperature of 800 °C was selected to study polymer-to-ceramic conversion and fiber morphologies. SiOC ceramic fibers mats were synthesized after pyrolysis.

Characterization

Characterization techniques were performed on raw, crosslinked, and pyrolyzed samples to determine chemical, mechanical, surface, and compositional changes of the mats at each stage. Fiber diameter and surface morphology were obtained via SEM (EVO MA10, ZEISS, Germany), and corresponding characteristics of fiber surface and cross sections were observed after focused ion beam (FIB) treatment in the SEM. XPS (K-alpha XPS/UPS photoelectron spectrometer, ThermoFisher, USA) was used for compositional analysis, and XPS survey and high-resolution scans were performed on fiber mats for a 10 s acquisition time with depth-profiling via 2 min Ar sputtering at 3 keV.

Techniques such as Raman spectroscopy (ARAMIS Raman spectrometer, LabRAM HORIBA Jobin Yvon, USA), FTIR (Spectrum 400 FT-IR spectrometer, Perkin Elmer, USA), and NMR spectroscopy were used to investigate the molecular structure of prepared fiber mats. Solid-state ¹³C CP MAS and ²⁹Si MAS NMR spectra were recorded on a Bruker AVANCE 300 spectrometer ($B_0 = 7.0$ T, $\nu_0(^1\text{H}) = 300.29$ MHz, $\nu_0(^{13}\text{C}) = 75.51$ MHz, $\nu_0(^{29}\text{Si}) = 59.66$ MHz) using a 7 mm Bruker probe and spinning frequency of 5 kHz. ¹³C CP MAS experiments were recorded with ramped-amplitude cross-polarization in the ¹H channel to transfer magnetization from ¹H to ¹³C (i.e., recycle delay = 3 s, CP contact time = 1 ms, optimized ¹H spinal-64 decoupling). Single-pulse ²⁹Si NMR MAS spectra were recorded with recycle delays of 60 s. Chemical shift values were referenced to preceramic precursors for ¹³C

and ^{29}Si . Raman spectra were collected using a HeNe laser (632 nm) to analyze free carbon in the pyrolyzed system; FTIR was performed using an attenuated total reflectance (ATR) setup and collected IR spectrums ranging from 500 to 3500 nm with 64 cumulation number that provided data from functioning groups at each stage. NMR revealed detailed bonding using various elements in each sample.

5.2 Results and discussion

Microstructure

SEM images of crosslinked and pyrolyzed fibers are presented in Figure 5.3. The fibers were initially drawn under identical conditions (15 kV, ~ 20 cm distance between needle and collector, sol-gel feeding speed of 5 ml hr^{-1}). Raw samples were uniform in diameter across the individual fibers. For 4-TTCS samples, the average fiber diameter was initially $3.5 \text{ }\mu\text{m}$, decreased to approximately $3.0 \text{ }\mu\text{m}$ after crosslinking, and then further shrunk to approximately $1.5 \text{ }\mu\text{m}$ (about 60 % shrinkage from raw fibers) after pyrolysis. Various Si initial compounds resulted in unique features of the pyrolyzed fibers. Average fiber diameters changed significantly from $3 \sim 5 \text{ }\mu\text{m}$ (for Pt-TTCS sample) to $1 \sim 3 \text{ }\mu\text{m}$ (for 4-TTCS and 3-TTCS samples) and $0.2 \sim 1.0 \text{ }\mu\text{m}$ (for DTDS sample). The results indicate that the crosslinking mechanism (by DCP or Pt) led to varied diameter distribution; furthermore, the large silicon compound (with higher average molecular weight) derived thick fibers for cyclic types of preceramic precursors. In addition, DTDS derived fibers were smoother (or less porous) on the fiber surface compared to the other three samples. Amorphous (nanodomain) structures of ceramic fibers were revealed by high-res TEM images (Figure 5.3 k-n), compare to the clear crystalline structure of nano Pt particles in Figure 5.3 l.

Cyclic precursors derived translucent fibers, revealing the possible hollow features of the fibers, which were also captured from the cross-sectional view. Theoretically, the formation of hollow structured fibers is primarily related to the spinning process¹⁶⁸. Research has shown that post-heat treatment on the core-shell structure creates hollow fiber mats via

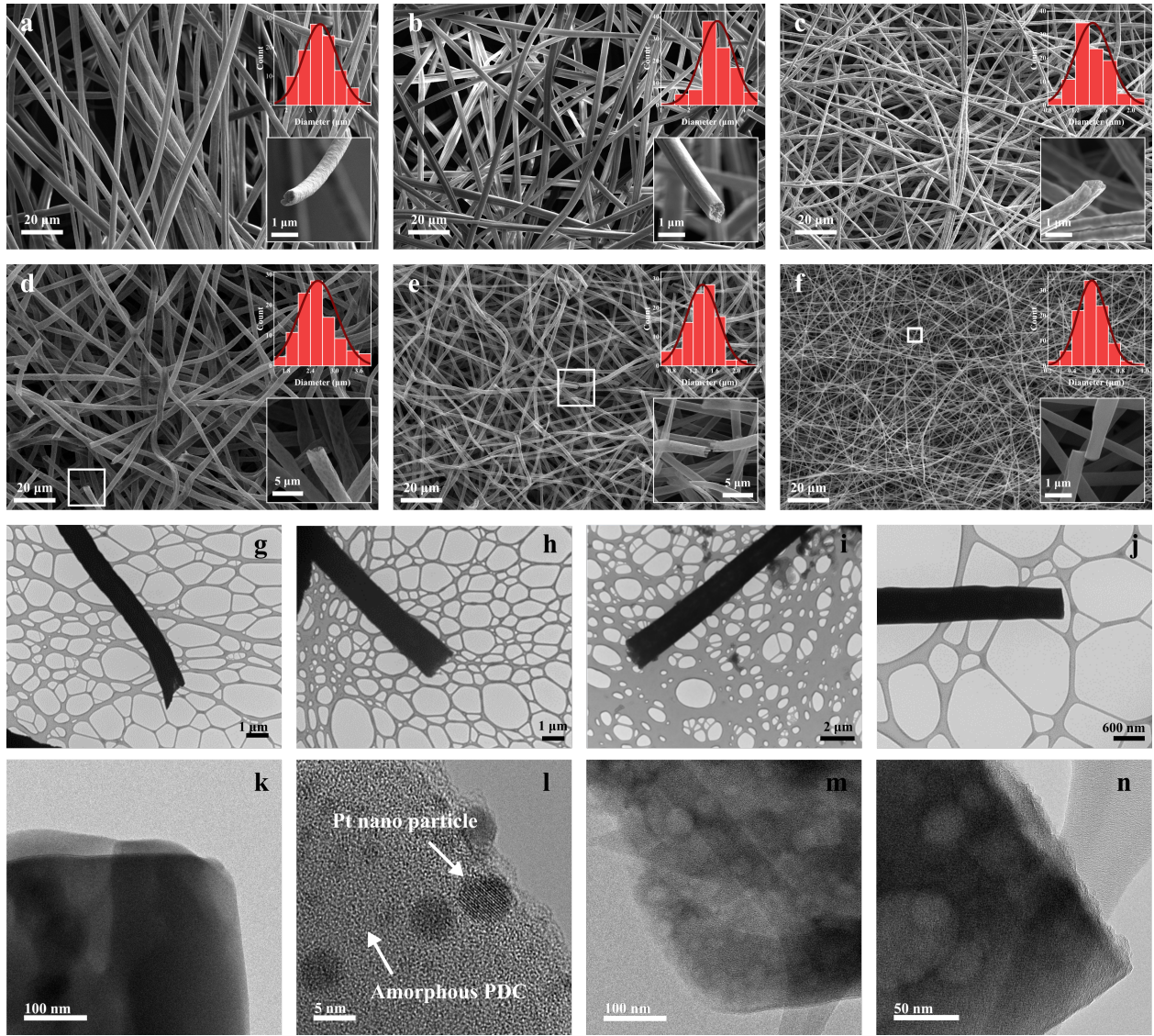


Figure 5.3: SEM, TEM images, and corresponding XPS spectra of electrospun fiber mats. SEM images of (a) 4-TTCS/PVP as spun; (b) 4-TTCS/PVP crosslinked at 160 °C; (c) 4-TTCS/PVP pyrolyzed at 800 °C; (d) Pt-TTCS/PVP pyrolyzed at 800 °C; (e) 3-TTCS/PVP pyrolyzed at 800 °C; and (f) DTDS/PVP pyrolyzed at 800 °C. Further magnified images are shown in the insets of (a)–(f). TEM images of (g) 4-TTCS/PVP pyrolyzed; (h) Pt-TTCS/PVP pyrolyzed; (i) 3-TTCS/PVP pyrolyzed; and (j) DTDS/PVP pyrolyzed. Corresponding high-res TEM images of (k) 4-TTCS/PVP pyrolyzed; (l) Pt-TTCS/PVP pyrolyzed; (m) 3-TTCS/PVP pyrolyzed; and (n) DTDS/PVP pyrolyzed.

electrospinning, where the core-shell structure could be formed if two different polymers were extruded simultaneously with two coaxial capillaries. However, in our case, the spinning solution was prepared by mixing preceramic silicon polymer, linear PVP polymer (as spinning

agent), and solvent. The as-prepared solutions were electrospun using a single syringe needle. Hence, we suspect the core-shell structure was formed during the spinning process due to the molecular weight difference between preceramic polymers and PVP ($\sim 1,300,000 \text{ g mol}^{-1}$). The small, or short, molecules demonstrated increased mobility when they were applied to the same electrostatic force that can be pulled out of the rigid PVP environment and form such hollowed structures. The holes were formed during heat treatments (i.e., crosslinking and pyrolysis). Further investigation of this phenomenon is needed with other characterization techniques.

Compositional analysis

Raman spectroscopy results (Figure 5.4) were used to determine carbon bonding and corresponding microstructures of 800 °C pyrolyzed systems. All samples, except Pt-TTCS/PVP, showed obvious carbon D band (around 1340 cm^{-1}) and G band (around 1600 cm^{-1}) absorptions in the spectra, which indicated the potential presence of a free-carbon or nanodomain structure. The curve-fitted result showed a considerable amount of disordered $\text{sp}^2\text{-sp}^3$ bonds (indicated by T band at $1204 \sim 1232 \text{ cm}^{-1}$) and amorphous carbon (D'' at $1490 \sim 1504 \text{ cm}^{-1}$) in the pyrolyzed samples^{48;104}. The Pt-TTCS/PVP sample showed strong fluorescence under visible (HeNe at 632 nm) and IR (diode at 785 nm) laser sources and no significant carbon D or G band in the structure. However, under a 532 nm laser source, the Pt-TTCS/PVP sample revealed carbon D and G bands, which were most obvious after the background was removed. The fluorescence may have been caused by Pt in the sample, as confirmed by XPS. FTIR spectra of raw, crosslinked, and pyrolyzed samples were collected for each type of sample (i.e., neat PVP and each PVP/preceramic silicon polymer). Table 1 Characteristic wavenumbers of different chemical groups for each preceramic silicon polymers and PVP.

Figure 5.5 shows FTIR results with marked characteristic absorption bands. Corresponding characteristic peaks are summarized in Table 3.1 for various preceramic silicon precursors and PVP. For neat PVP samples, a comparison between raw and 160 °C heated samples (neat PVP XL) showed that all the samples retained main peaks for PVP (C-O at $\sim 1650 \text{ cm}^{-1}$,

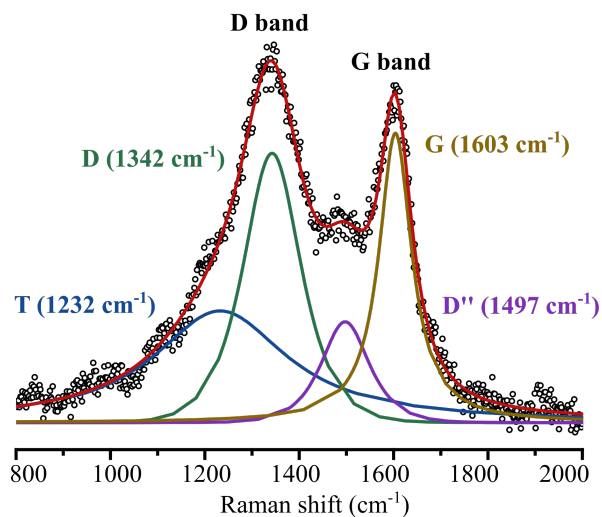
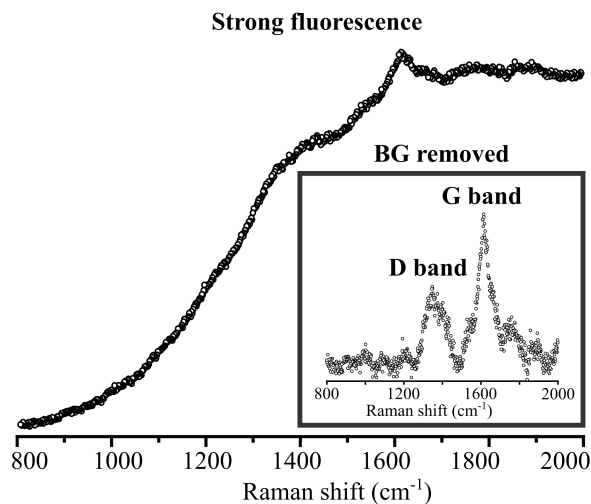
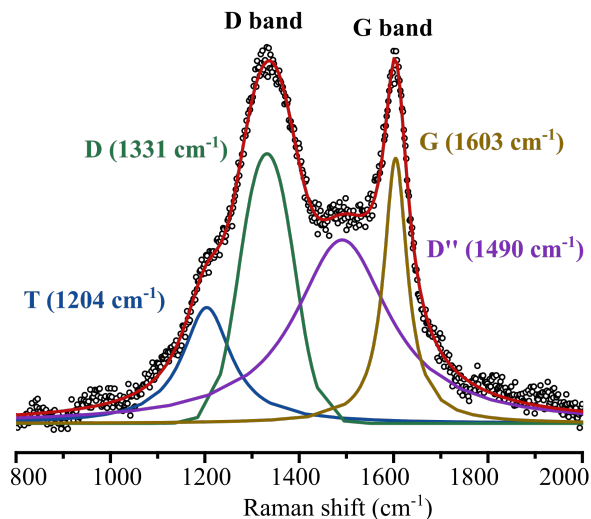
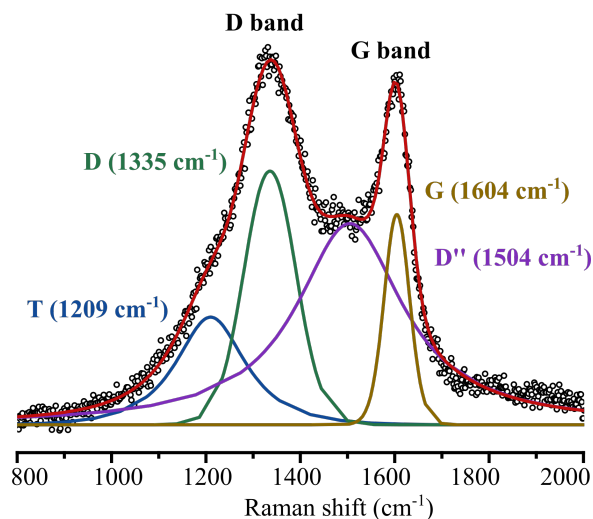
a 4-TTCS/PVP 800**b Pt-TTCS/PVP 800****c 3-TTCS/PVP 800****d DTDS/PVP 800**

Figure 5.4: Raman spectra of pyrolyzed fiber mats with integrated peaks shown in the plot. a) 4-TTCS/PVP; b) Pt-TTCS/PVP sample with strong fluorescence. The spectrum with a removed background is shown in the inset; c) 3-TTCS/PVP; d) DTDS/PVP.

C-H at ~ 1420 cm⁻¹ and N-C=O at ~ 570 cm⁻¹), suggesting that no obvious crosslinking reaction occurred. The high-temperature pyrolysis of heat treated neat PVP in an inert atmosphere was performed to confirm this finding. Destruction of the fiber mat suggested no or low crosslinking during the low-temperature heat treatment. When PVP was mixed with 4-TTCS or Pt-TTCS, very strong peaks, such as Si-O-Si at ~ 1059 cm⁻¹, Si-CH=CH₂ at ~ 1000 cm⁻¹, and Si-CH₃ ~ 750 cm⁻¹, which did not exist in neat PVP samples, were observed.

Table 5.1: *Characteristic wavenumbers of different chemical groups for each preceramic silicon polymers and PVP.*

	Wavenumber (cm ⁻¹)	Chemical group	Ref
PVP	3399	OH stretching	169
	2918	CH ₂ asymmetric stretching	169
	1648	C-O stretching	169
	1422	CH bending	169
	1288	CH ₂ wagging	169
	1018	CH ₂ rock	169
	570	N-C=O bending	169
4-TTCS	3057, 3016	Si-CH=CH ₂ (CH asymmetric stretching)	143
	2964	Si-CH ₃ (CH symmetric stretching)	143
	1598	Si-CH=CH ₂ (C=C stretching)	143
	1408	Si-CH ₃ (C-H asymmetric bending)	143
	1260	Si-CH ₃ (C-H symmetric bending)	143
	1059	Si-O-Si asymmetric stretching	143
	1007, 959	Si-CH=CH ₂ (CH out-of-plane bending)	143
	789, 746	Si-CH ₃ (Si-C deformation vibration)	170
	682, 645	Si-CH ₃ (Si-C stretching)	143
3-TTCS	2950	CH ₂ asymmetric stretching	171
	1662	Si-CH=CH ₂ (C=C stretching)	171
	1424	Si-CH ₃ (C-H asymmetric bending)	171
	1288	Si-CH ₃ (C-H symmetric bending)	171
	1020	Si-O-Si (Siloxane stretch)	171
	803, 744	Si-CH ₃ (CH ₃ rock)	171
DTDS	2954	CH ₂ asymmetric stretching	172
	1660	Si-CH=CH ₂ (C=C stretching)	172
	1423	Si-CH ₃ (C-H asymmetric bending)	172
	1288	Si-CH ₃ (C-H symmetric bending)	172
	1058	Si-O-Si (Siloxane stretch)	172

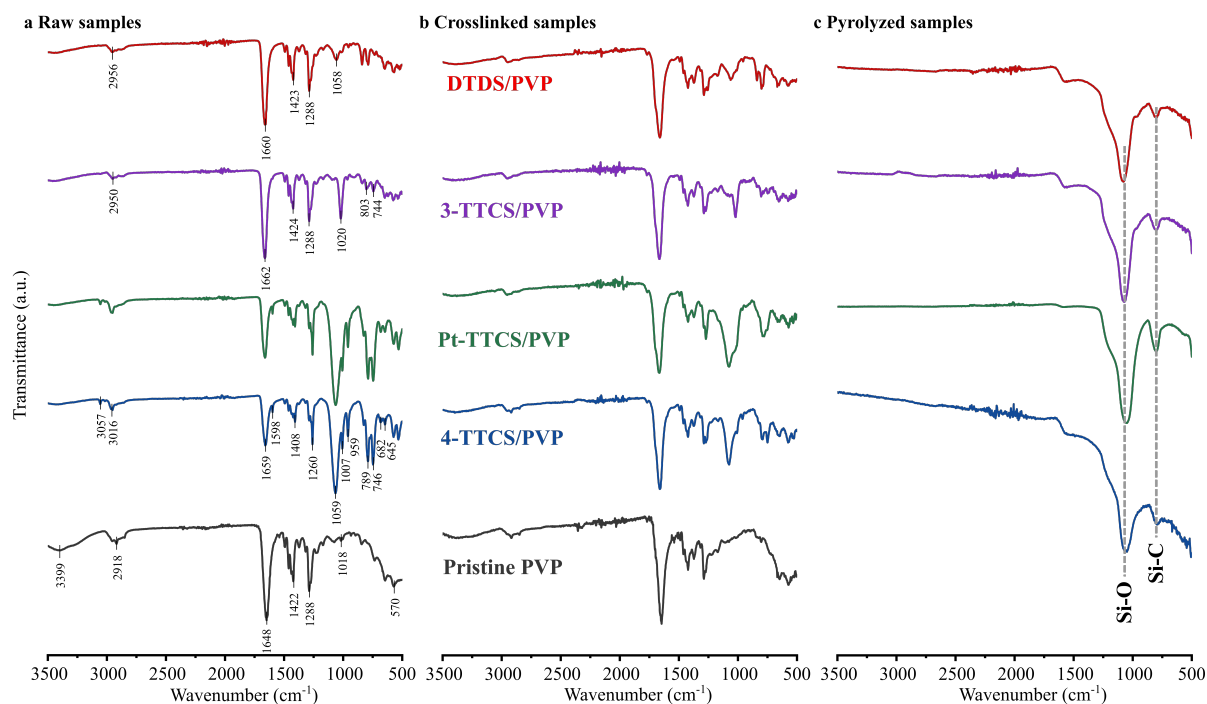


Figure 5.5: FTIR spectra of raw, crosslinked, and pyrolyzed electrospun siloxane/PVP and pristine PVP fiber mats. Major peaks of pyrolyzed samples are marked within the plot.

After crosslinking at 160 °C, decreased Si-CH=CH₂ and Si-CH₃ peaks indicated a strong crosslinking reaction of TTCS, and after pyrolysis, the spectrum showed the decomposition of PVP organic components and the retention of Si-O in the system. Although 3-TTCS molecules are structurally resemble to 4-TTCS molecules, 3-TTCS samples showed a unique spectrum that the characteristic peaks were less intense even though similar crosslinking behavior was observed from the decrease of Si-CH=CH₂ at 1662 cm⁻¹ and Si-CH₃ at 1424 and 1288 cm⁻¹. Relatively weaker crosslinking evidence was observed in the DTDS sample with less obvious changes of Si-CH₃ at 1424 and 1288 cm⁻¹ after crosslinking. As shown in Figure 5.5c, all pyrolyzed samples had strong absorptions at the Si-O (~ 1050 cm⁻¹) peak and weak absorptions at the Si-C (~ 700 cm⁻¹) peak. The relatively strong Si-O absorption indicated the presence of more Si-O than Si-C bonds in all samples.

XPS survey scans were performed on pyrolyzed fiber mats to investigate the sample compositions. Elemental compositions (Table 3.2) of pyrolyzed samples differed significantly for each preceramic polymer. The atomic weight percentages were calculated by integrating

Table 5.2: *Elemental composition by XPS.*

Pyrolyzed samples	Elements (at. %)				Empirical formula
	Si	C	O	Pt	
4-TTCS/PVP	23.7	41.5	34.8		SiC _{1.75} O _{1.47}
Pt-TTCS/PVP	41.1	13.4	44.9	0.6	SiC _{0.33} O _{1.09} Pt _{0.01}
3-TTCS/PVP	38.4	13.8	47.8		SiC _{0.36} O _{1.24}
DTDS/PVP	29.0	31.8	39.2		SiC _{1.10} O _{1.35}

the areas under critical peaks. The Pt-TTCS/PVP sample derived the highest Si composition (41.1 at. %) with the highest O (44.9 at. %) and lowest C contents (13.4 at. %). However, 4-TTCS/PVP, which had the same initial structure as Pt-TTCS, produced a final composition with the lowest Si (23.7 at. %) and highest C (41.5 at. %). Similarly structured 3-TTCS (6-ring cyclic siloxane) provided a similar composition to Pt-TTCS/PVP, while DTDS/PVP demonstrated a balanced chemical composition after pyrolysis. As mentioned, the Si and O had identical initial atomic percentages in 4-TTCS, Pt-TTCS, and 3-TTCS preceramic silicon polymers, and Si:O = 2:1 in DTDS. Therefore, the inference was made that all polymers gained oxygen during the heat treatments.

Si, C, O, and high-resolution scans (shown in Figure 5.6) were conducted for the samples to determine the bonding of each sample. The bonding types of Si must be determined to accurately estimate the microstructures of the fiber mats. Stacked high-resolution scans showed shifting peaks according to initial compositions of preceramic polymers, revealing a variation of integrated peaks. Multi-peak fittings were performed to all high-resolution scans with marked integrated peaks^{104;118}: SiO₄ (104.5 ± 0.1 eV), SiCO₃ (103.5 ± 0.1 eV), SiC₂O₂ (102.9 ± 0.1 eV) for Si2p; C=O (287.1 ± 0.1 eV), C-C (284.9 ± 0.1 eV), C-Si (284.0 ± 0.1 eV) for C1s; C=O (534.4 ± 0.1 eV), O-Si (532.9 ± 0.1 eV), SiO₂ (532.4 ± 0.1 eV) for O1s. Pt4f high-res XPS is recorded and presented in Figure 5.7 from the same fiber mat that the survey scan and other (O1s, C1s and Si2p) high-res are performed. As shown, the deconvoluted peaks are shown and marked with corresponding oxidation status at Pt⁰ (70.9 eV), PtO (72.0 eV) and PtO₂ (73.2 eV). The following Solid-state NMR spectroscopy was performed on pristine PVP, crosslinked siloxane/PVP, and pyrolyzed samples. Bulk powder samples

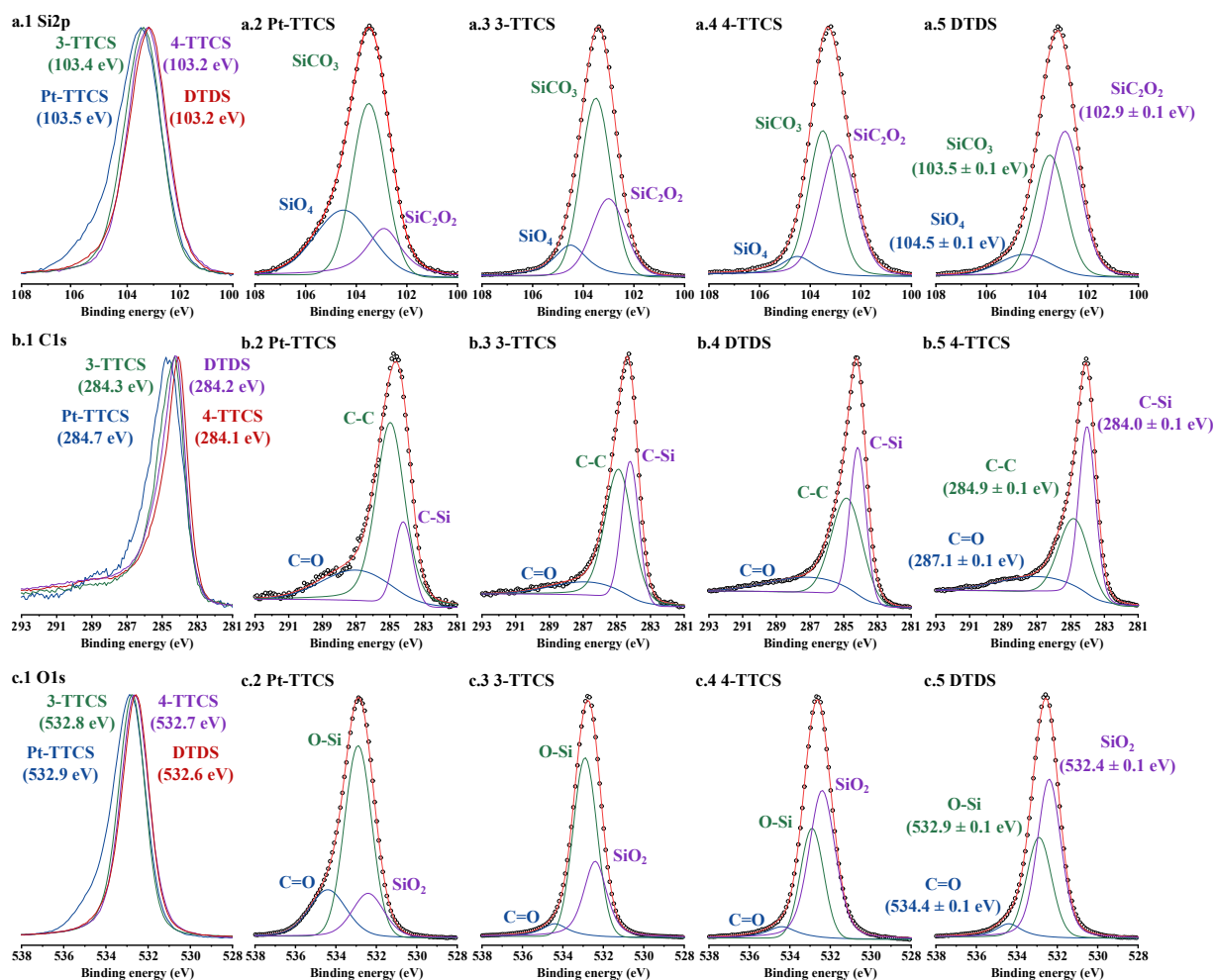


Figure 5.6: XPS spectra of all pyrolyzed fiber mat samples with various preceramic polymer precursors with plots of high-resolution scans of Si2p, C1s, and O1s. The first column shows stacked high-resolution scans (normalized to 4-TTCS) of a.1) Si2p: b.1) C1s: and c.1) O1s, with peak centers marked. Subplots of columns 2–5 show integrated peaks with marked components.

were used to enhance the NMR signal. From the ^{29}Si MAS analysis of crosslinked samples, ring structures of both the reserved 8- (around 32 ppm for 4-TTCS samples)^{135;136} and 6-units (around 23 ppm for 3-TTCS)¹⁷³ were detected after crosslinking. Also, the formation of broad $-\text{CHx}-\text{MeSiO}_2$ (for 4-TTCS and 3-TTCS samples) and $-\text{CHx}-\text{Me}_2\text{SiO}-$ (for DTDS sample)¹⁷⁴ peaks indicated a rigid crosslinked phase by DCP after heat treatment at 160 °C. Similarly, a less-effective crosslinking reaction of Pt suggests that DCP is more efficient for this type of cyclic siloxane. ^{29}Si MAS NMR spectra of pyrolyzed samples showed the highest

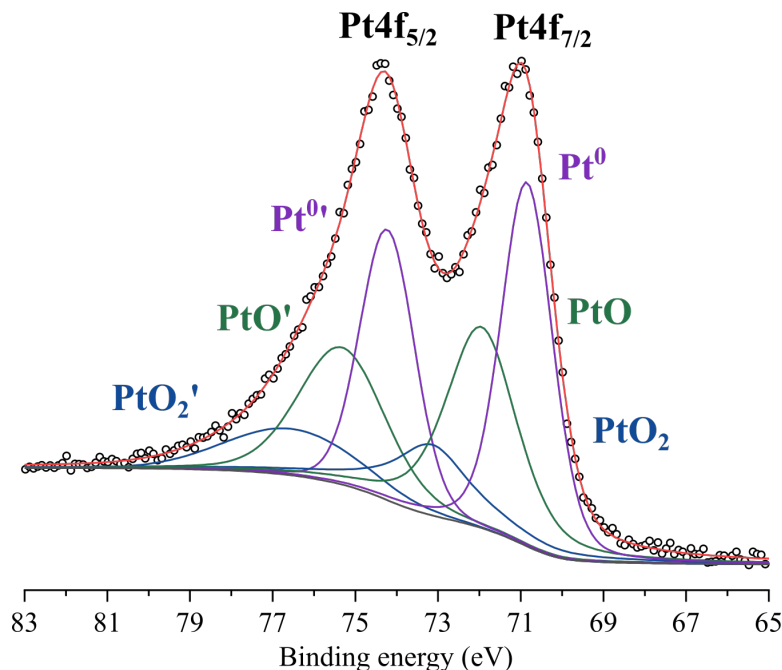


Figure 5.7: *High resolution XPS Pt_{4f} scan of Pt-TTCS/PVP pyrolyzed mat.*

amounts of SiC_2O_2 and SiCO_3 , indicating high Si-C contents in the 4-TTCS sample, and less SiCO_3 in the 3-TTCS sample, as well as almost no Si-C related peaks in the Pt-TTCS sample. XPS analysis also confirmed low carbon content in the Pt-TTCS/PVP sample. The ^{29}Si MAS spectrum was not obtainable from the pyrolyzed DTDS sample due to the formation of radicals in the free carbon phase. The significant Si-CH_x characteristic peaks on the ^{13}C CP MAS NMR spectra of crosslinked samples imply that 4-TTCS and 3-TTCS samples had the highest siloxane-to-PVP ratio after crosslinking. The remaining $-\text{CH}=\text{CH}_2$ signals suggest incomplete crosslinking of $\text{C}=\text{C}$ that may occur due to the limited mobility of siloxane molecules in the PVP environment during crosslinking. Nonetheless, the weak $-\text{CH}=\text{CH}_2$ signal in the DTDS sample demonstrated more complete crosslinking because of the improved mobility of the small molecules. This finding was consistent with the relatively high numbers of XPS-detected SiC_2O_2 groups.

NMR spectra of samples pyrolyzed at 1000 °C. As the increase of pyrolysis temperature, increase of SiC_2O_2 and SiCO_3 structures were observed only in 3-TTCS sample. However, almost unchanged microstructures were shown for 4-TTCS and Pt-TTCS samples.

Combining all the evidences, the compositional analyses of crosslinked and pyrolyzed

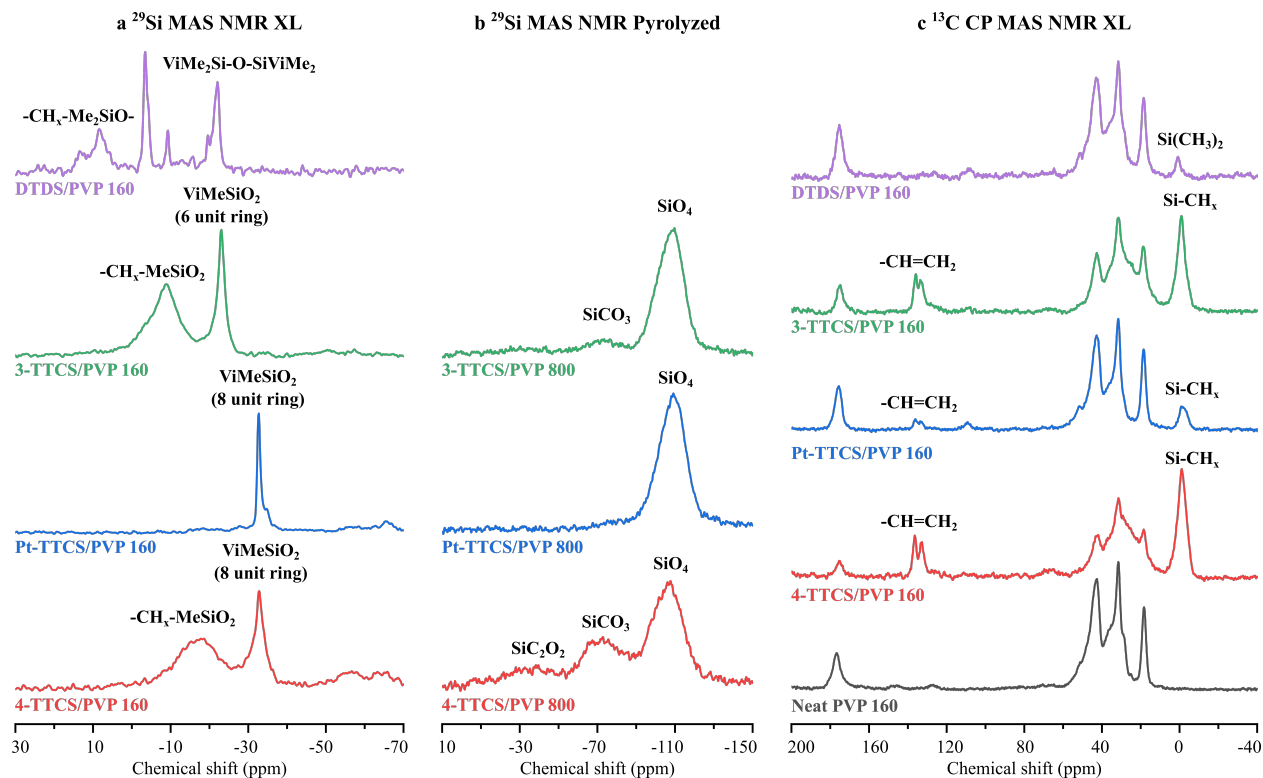


Figure 5.8: Solid-state NMR spectra crosslinked and pyrolyzed fiber mats. (a) ^{29}Si MAS NMR XL; (b) ^{29}Si MAS NMR pyrolyzed; and (c) ^{13}C CP MAS NMR XL.

fiber mats revealed the strong crosslinking reactions between preceramic precursors. Precursors, that were initially embedded in the PVP environment, crosslinked through vinyl and methyl groups. This process corresponds to the widely agreed crosslinking mechanisms of Si compounds (as shown by equation 1 and 2 in Experimental section), and was confirmed by the decrease of $\text{Si}-\text{CH}=\text{CH}_2$ and $\text{Si}-\text{CH}_3$ FTIR signals (Figure 5.5 a, b) and formation of low mobile $-\text{CH}_x-\text{Me}_2\text{SiO}-$ NMR signals (Figure 5.7 a).

Structurally, PVP molecules do not have a potential crosslinking site with Si compounds. Pristine PVP fiber mats also failed to survive 800 °C pyrolysis, that indicates no crosslinking behaviour of PVP molecules. In addition, FTIR and NMR of crosslinked fiber mats indicated no or weak interactions between the precursor molecules and spinner PVP molecules. FTIR spectra of pristine PVP sample showed slight decrease of C-H and CH_2 signals, which might due to the thermal decomposition of the molecule. However, when precursors were added to the system, characteristic peaks of PVP did not show a further decrease. ^{13}C CP MAS

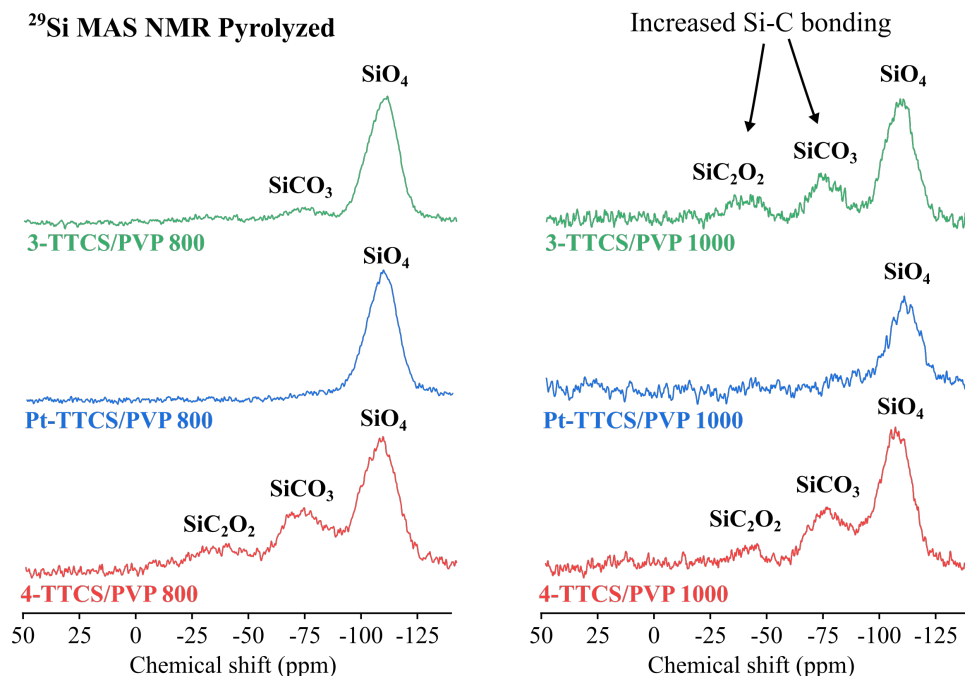


Figure 5.9: ^{29}Si MAS NMR spectra of samples pyrolyzed at 800 °C and 1000 °C.

NMR spectra of PVP and hybrid samples (Figure 5.7 c) also showed all reserved PVP peaks. The spinner PVP molecules are expected to decompose at pyrolyzing temperature and contributes to excessive or free carbon phase.

Mechanical Properties and Thermal Stability

Nanoindentation was performed (results plotted in Figure 5.10) on fiber surfaces that were embedded in epoxy resin in the pyrolyzed 4-TTCS/PVP sample. Results of the indentation revealed the fiber transverse modulus of 5.6 GPa (1.84 GPa for epoxy resin). In addition, all the fiber mats were directly exposed to an acetylene torch flame for 20 s (Figure 5.8); the XPS analysis results are shown in Table 3.3. Under an oxidizing high-temperature environment, the Pt-TTCS/PVP sample did not show any changes, while the 4-TTCS/PVP and 3-TTCS/PVP mats demonstrated slight oxidation at the surface (i.e., turned gray after heat treatment). However, the DTDS/PVP samples shrunk and turned completely gray, suggesting the lowest oxidation resistance among the four tested samples. XPS analysis revealed compositional changes after exposure to the flame. The Pt-TTCS/PVP sample showed

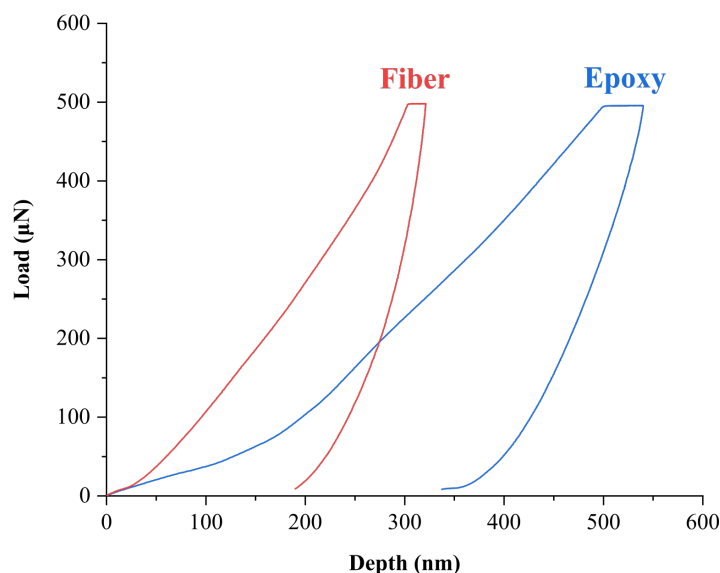


Figure 5.10: *Nanoindentation result of 4-TTCS/PVP pyrolyzed mat embedded in epoxy. The plot shows two individual indentation on a single ceramic fiber and the hard epoxy resin surrounding the fiber.*

almost unchanged composition but slightly decreased Si content, while the 4-TTCS/PVP and 3-TTCS/PVP samples showed minimal changes with slightly decreased carbon content compared to previous

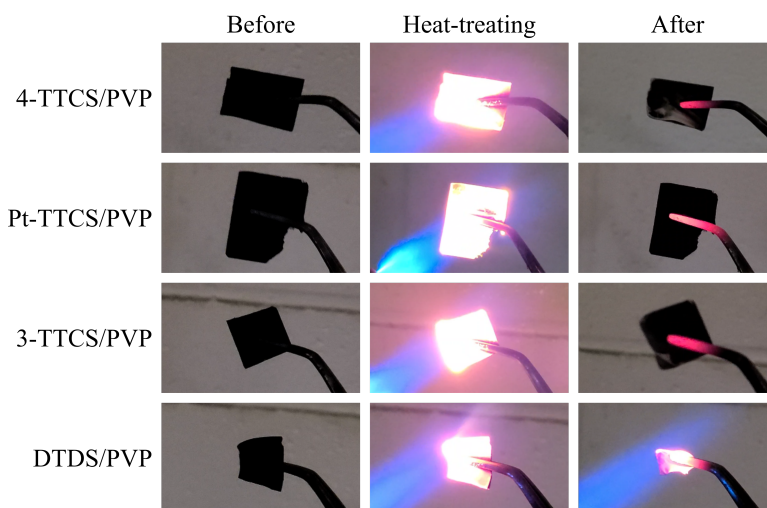


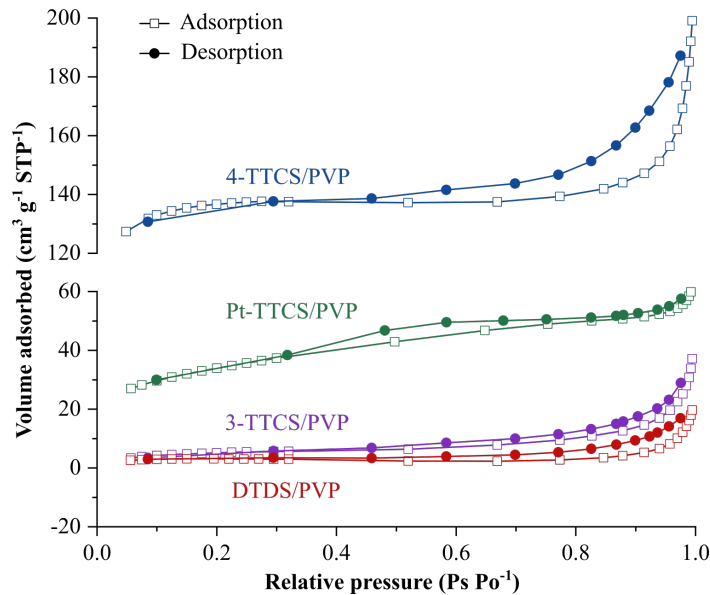
Figure 5.11: *Four types of fiber mats directly exposed to acetylene flame torch.*

XPS data. The DTDS/PVP sample showed critically decreased carbon content (from 31.8 % to 6.8 %), which resulted in shrinkage of the fiber mat.

Table 5.3: *Elemental composition by XPS after exposure to acetylene flame.*

Pyrolyzed samples	Elements (at. %)			
	Si	C	O	Pt
4-TTCS/PVP	24.0	39.5	36.5	
Pt-TTCS/PVP	40.8	16.9	41.9	0.4
3-TTCS/PVP	40.7	13.4	45.9	
DTDS/PVP	40.6	6.8	52.5	

Flame torch tests suggest a relation between microstructures and thermal stabilities. The best, performing Pt-TTCS sample was previously revealed with highest SiO_4 bonding character (from NMR and XPS) and highest Si-O bonding (from XPS). 3-TTCS sample with slightly higher SiCO_3 content showed a slight decrease in thermal stability. Consecutively, 4-TTCS, with slight SiC_2O_2 and significant SiCO_3 structure, showed further decreased thermal stability from 3-TTCS. While, microstructure and NMR information related to DTDS was not as conclusive. It did however show the least stability to flame torch.

**Figure 5.12:** *BET surface area analyses of pyrolyzed fiber mats.*

BET surface area analyses were performed on as-spun ceramic fiber mats. N_2 is used as analysis adsorptive. The adsorption curves are plotted in Figure 5.12. As a result, the

BET surface area and the adsorption pore sizes were calculated and provided in the Table 5.4. As seen from the results, 4-TTCS/PVP sample showed the highest BET surface area. Besides, all four samples exhibited type II isotherm, which indicated macro pores within the structures. The adsorption hysteresis of all four samples strongly suggest the network pore structures existing in the samples, this may caused by the structural porosity of the electrospun fiber mats.

Table 5.4: *Elemental composition by XPS after exposure to acetylene flame.*

Pyrolyzed samples	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Adsorption pore size (nm)
4-TTCS/PVP	416.7	2.3
Pt-TTCS/PVP	115.6	2.8
3-TTCS/PVP	18.3	6.2
DTDS/PVP	9.2	5.0

5.3 Conclusions

This study used electrospinning to synthesize SiOC fiber mats from four preceramic silicon oligomers and PVP hybrid spinning precursors. Electrospinning efficiently and reliably produced large fiber mats. As-spun fiber mats were subjected to two- stage heat treatment for complete polymer-to-ceramic conversion. During cross-linking and pyrolysis, the fiber surfaces changed from smooth to highly porous. Each preceramic oligomer derived unique final SiOC compositions even if the initial structures were very similar for 4-TTCS, Pt-TTCS, 3-TTCS, and DTDS, proving the controllability of final compositions. Characterization results revealed the porosity of the pyrolyzed 4-TTCS, Pt-TTCS, and 3-TTCS samples. Small DTDS molecules resulted in dense, thin fibers, while surface compositional analyses showed preserved Si composition at the fiber surfaces. Improved thermal crosslinking reactions were achieved via DCP, although Pt was shown to increase final Si composition. In the thermal stability tests, Pt-TTCS demonstrated the overall best stability under oxidizing conditions. The Pt-TTCS, 4-TTCS, and 3-TTCS samples showed only slight compositional changes af-

ter heat treatment, and only the DTDS sample showed significant shrinkage and carbon loss after heat treatment.

In conclusion, when electrospinning PDC fibers with a precursor that is initially not spinnable, spinning reagents can be added to provide viscosity and enable electrospinning, as when PVP was used in this study. The PVP molecules showed neither a crosslinking behaviour of its own, nor crosslinking interactions with all precursor molecules. The amount of spinning agent is critical to spinnability of the hybrid precursor system, in case for PVP, 400 wt. % maximum loading (precursors to PVP = 4:1) were achieved for all precursors. Different preceramic precursors and crosslinking catalysts affected the final compositions and microstructures, therefore, further influenced thermal stabilities of the final PDC fiber mats. Lower excessive free carbon phase and higher Si-O bonding resulted in better thermal performance under acetylene flame torch.

Chapter 6

Conclusion and Future Work

6.0.1 Summary

This research used novel techniques to synthesize and characterize PDC fibers. Fiber bundles, individual fibers and fiber mats were obtained, and the developed techniques produced long, uniform fibers from preceramic precursors. Compared to commercial manufacturing techniques such as melt spinning or wet spinning, these techniques required minimum setup without long production lines or continuous heat treatments during the production, thereby simplifying fiber production in lab and reducing manufacturing costs.

Chapter 1 introduced the current status of PDCs and their properties and applications, specifically, PDC fibers and commercial CMC applications. Chapter 2 described spinning setups that were used to carry out the research, including the synthesis process, essential parameters and correct way to improve the spinning of preceramic precursors.

Chapter 3 introduced hand spun ceramic fibers from cyclic precursor for the first time and investigated fiber morphologies using various microscopic techniques, which suggested hand spun fibers have smooth surface features and uniform diameters with narrow distributions. Compositional analysis showed reserved silicon contents after crosslinking and pyrolysis, and spectroscopic techniques revealed chemical changes during crosslinking and pyrolysis indicating the decomposition of fiber template (linear polymer) and the formation of amorphous ceramic phases with excessive carbon.

Chapter 4 applied electrospinning to four types of similarly structured silicon precursors. The overall structure resembled the precursor used in hand spinning. Fiber mats were prepared from all four precursors under identical engineering parameters; the prepared fibers had diameters ranging from several microns down to hundreds of nanometers. Fiber diameter distribution was well controlled via the electrospinning technique. Final compositional analysis showed higher silicon concentration than hand spun fibers, and results of the mechanical test and thermal stability test showed good potential for high temperature applications.

6.0.2 Suggested Future Work

Although the PDC fibers were successfully prepared in various ways and characterization revealed the fiber chemical composition, fiber morphology, fiber thermal stability, and most of the chemistry behind the entire polymer-to-ceramic conversion process, further investigation of fiber mechanical properties at room temperature and elevated working temperatures, must be conducted to determine the full potential of the ceramic fibers in real applications.

1. Tensile strength testing setup for fiber bundles or individual fibers Chapter 1 introduced fracture mechanisms of the CMC in which fiber strength and modulus enhance fracture toughness of the CMC. However, properties of the products in the form of not only fully CMC, but fibers as well must be determined, and the mechanical testing techniques must be conducted under room temperature and high temperatures (above 1000 °C). For example, tensile testing could be conducted in lab scale if the tensile testing occurs in a vacuum chamber with a built-in IR local heating setup so only the center of the target is heated in seconds and tensile testing occurs at desired temperature.

2. Manufacturing of CMC Once the properties of ceramic fibers are fully understood, the production of CMCs with prepared fibers is inevitable since these fibers are made for high-temperature applications. Therefore, polymer matrix composites may first be produced with these fibers or fiber mats, and then CMCs can be produced with more complicated methods, such as CVI and PIP for lab-scale manufacturing presented in Chapter 1.

3. Ceramic fibers for other applications In addition to CMC reinforcement, ceramic fibers or fiber mats could be used to separate small particles at high temperatures in highly corrosive environments. They could also be used as precursors for ceramic- derived carbons, high-temperature catalysts or catalyst carriers, or various applications in energy storage. Because PDCs have already shown outstanding electrochemical energy storage performance as anode materials, carbon-rich ceramic fiber mats could serve as standalone anodes for batteries or supercapacitors.

4. Compatibility of the fiber drawing techniques to other types of preceramic polymers This research demonstrated fiber spinning from low molecular weight silicon oligomers using linear polymers. However, other types of precursors, such as linear silicon polymers, may require less or no carbon-based linear polymers. Moreover, precursors may be mixed to tweak the spinning, crosslinking and pyrolysis properties. Instead of using linear carbon polymers, linear silicon-based polymers may increase the final silicon concentration.

5. Synthesis of preceramic precursors with desired properties Future students with strong backgrounds in chemistry or chemical engineering could synthesize unique polymers in the laboratory to prepare precisely designed PDCs from monomer molecules level. Further functionalization could be realized by incorporating other elements.

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