Effect of Preceramic Oligomer Ring Size on the Processing of Polymer-Derived Si-C-N-O Fibers

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Abstract

Ceramic fibers were developed by hand spinning, crosslinking, and pyrolyzing a gel made from 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane (3TTCSZ) and polyacrylic acid (PAA) as a spinning agent. From here, we studied the crosslinking and pyrolysis behavior of the SiOCN ceramic fibers using Raman spectroscopy, Fourier- Transform InfraRed spectroscopy (FTIR), and X-ray Photoelectron Spectroscopy (XPS) to establish the cross-linking and pyrolysis mechanisms of the fibers.

Background and Motivation

- Silicon base non-oxide ceramic fibers such as SiC generally show good thermal stability, and superior mechanical strength at high temperature compared to oxide ceramic fibers
- Silicon base non-oxide ceramic fibers are exclusively prepared via the polymer pyrolysis route. One major obstacle for the application of such fibers in industry is the high material coast of the fiber (~$11000/ kg)
- The goal of this study was to study fabrication and characterization of polymer-derived ceramic fibers by hand-spinning low-cost oligosilazanes for potential use as reinforcement in ceramic matrix composites (CMCs).

Procedure

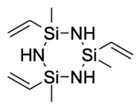

Figure 1: Chemical Structure of the Preceramic Oligomer
1,3,5-trivinyl-1,3,5-trimethlycyclotrisilazane **(3TTCSZ)**
*1% wt. Dicumyl Peroxide (DCP) as catalyst

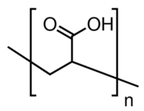

Figure 2: Schematic of Spinning Agent
polyacrylic acid **(PAA)**

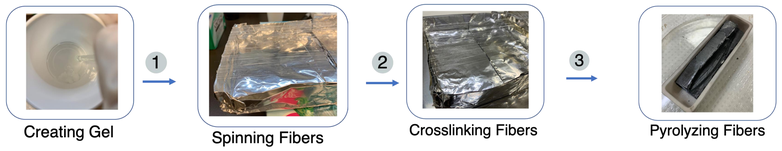

Figure 3: Schematic showing the fiber spinning process

Scanning Electron Microscopy

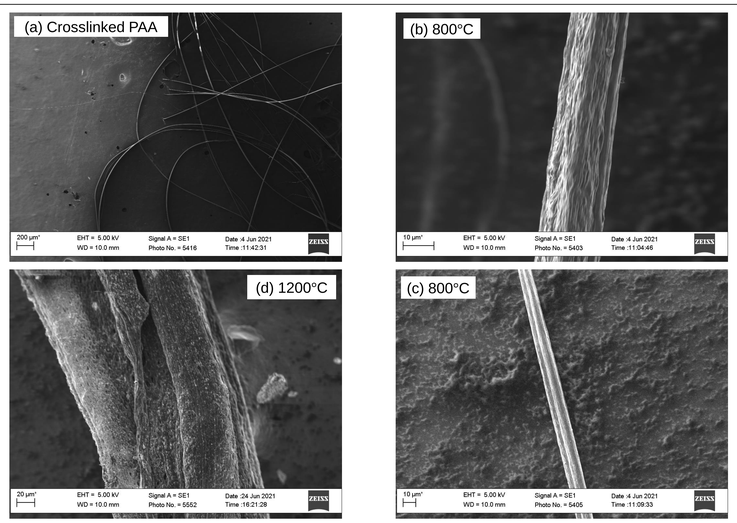

Figure 4: (a) Crosslinked PAA fibers, used as a base sample, (b) Ceramic fiber pyrolyzed at 800°C, surface view, (c) Long, uniform ceramic fiber pyrolyzed at 800°C, (d) Ceramic fiber pyrolyzed at 1200°C

Raman Spectroscopy

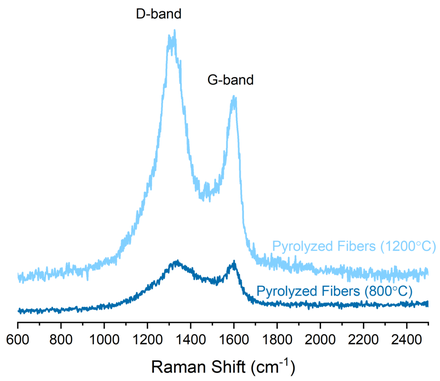

Figure 5: Raman spectra of pyrolyzed fibers

- Nondestructive tool to characterize the "carbon" phase in pyrolyzed ceramic fibers
- Allows us study the evolution of the "free" carbon phase in our sample
- D-Band represents disordered carbon
- G-Band represents ordered, or graphitic, carbon
- In samples pyrolyzed at lower temperatures (i.e. 800°C or less), several bands tend to overlap, the spectrum is broad, and the microstructure cannot be resolved
- For specimen pyrolyzed at higher temperatures, the well-defined D and G bands emerge suggesting the arrangement of carbon atoms in the form of ordered graphene sheets.

X-Ray Photoelectron Spectroscopy

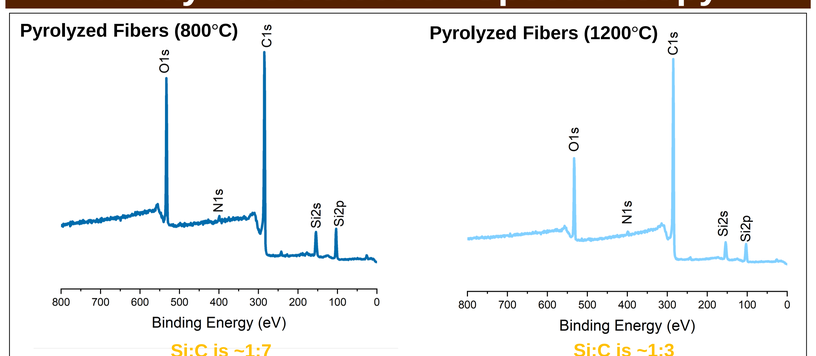

Figure 6: XPS survey scans of pyrolyzed fibers

- X-Ray Photoelectron Spectroscopy (XPS) is a technique in which a monochromatic X-Ray is incident on the sample resulting in ejection of photoelectrons
- A detector collects the number and kinetic energy of the electrons, allowing one to calculate the chemical binding energies of various compounds/elements in the sample
- Allows us to determine the composition and bonding types for the pyrolyzed ceramic fibers
- Presence of Si, C, N, and O elements in the spectrum confirms ceramization of the fibers.

Experience at Kansas State University

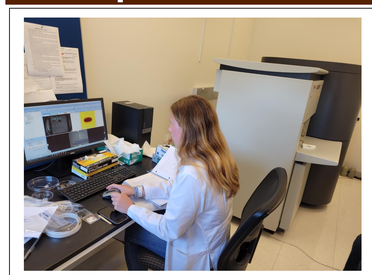

Figure 9:
Operating the XPS at University of Nebraska Lincoln (UNL) to obtain data for my samples

Figure 7: Working with the other students in the lab at Kansas State University (K-State)

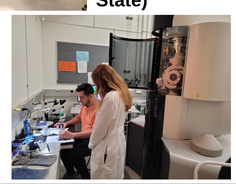

Figure 8: Preparing a sample for TEM at UNL with Davi, a graduate student from K-State

Fourier Transform Infrared Spectroscopy

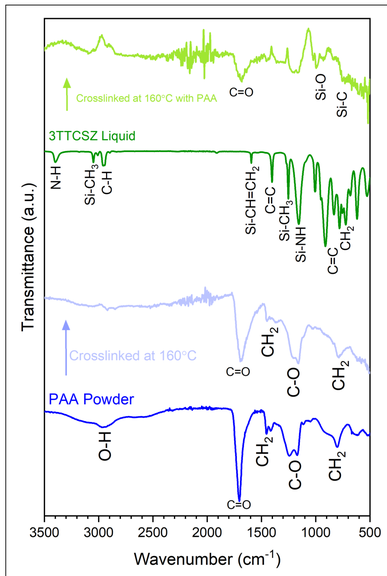

Figure 10: FTIR spectra before and after crosslinking

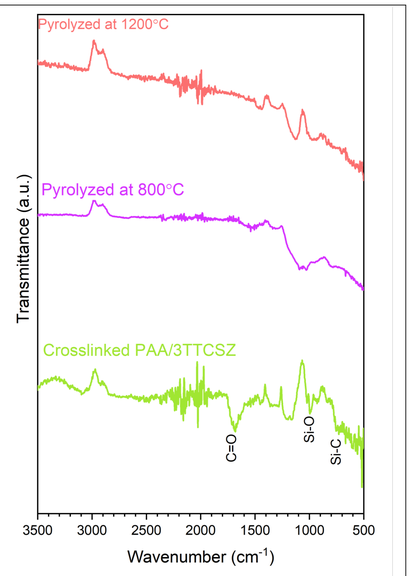

Figure 11: FTIR spectra of crosslinked and pyrolyzed fibers

- Fourier Transform Infrared Spectroscopy (FTIR) is a technique which detects all wavelengths in the infrared region absorbed by the sample
- Allows us to determine the organic functional groups present in the sample and how they evolve as the preceramic polymer is crosslinked and pyrolyzed (crosslinking mechanisms)
- As shown in Figure 10, the FTIR spectrum of liquid preceramic polymer confirms the molecular structure of the oligosilazane provided by the manufacturer
- The disappearance or reduction in the intensity of N-H, and Si-CH_3 suggests crosslinking via either dehydrogenation and/or evolution of CH_4 groups
- Emergence of Si-O band in the cross-linked specimen suggests ring opening and replacement of N by O during crosslinking in air
- Decrease in the intensity of Si-CH=CH_2 band upon crosslinking suggests contribution to polymerization via vinyl groups.

Conclusions and Future Work

The hand spinning fiber experiments showed that the optimal ratio of preceramic polymer to be added is 33% wt. in the PAA water solution and that the smaller size of the oligomer ring (as compared to previous works on (4TTCSZ) has increased spinnability at the cost of more brittle fibers. From the data analysis, it can be confirmed that the fibers produced were ceramic and contained the free or excess carbon phases. Further testing should be done to perfect the recipe of the 33% wt. fibers; specifically, the amount of water added during gelation. Additionally, more testing should be done to investigate the effect of the pyrolysis temperature on the amount "free" carbon phase present in the samples. Additionally, I look forward to traveling to Sorbonne University to perform Nuclear Magnetic Resonance (NMR) analysis on my samples to study the structural evolution.

Acknowledgements

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