Investigation of Cross-linking Mechanisms and the Evolution of Carbon Phase During Pyrolysis of Linear Oligosiloxanes

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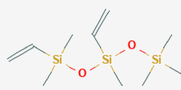
PIRE — SYNTHESIS • NANOSTRUCTURE • PROPERTIES — POLYMER-DERIVED CERAMIC FIBERS

Introduction and Objective

Polymer derived ceramics (PDCs) are promising ceramic materials which provide many efficient industrial applications and continue to increase in interest and research[1]. Free carbon, which has varying characteristics depending on precursor structure, can have significant impacts on the properties and applications of PDCs, due to its presence in the PDC microstructure. By controlling the amount of free carbon found in PDCs, further improvement of properties and applications of PDCs, as well as the introduction of new applications can be done[4].

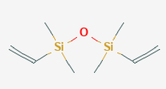
Analysis has been performed on neat precursor, crosslinked, and pyrolyzed polysiloxanes (SiOC following ceramization) to confirm the polymer to ceramic conversion as well as investigate the bonding and crosslinking mechanism. Precursors used in this research are: (a) TPTS [135trivinyl-11355pentamethyltrisiloxane 95%], (b) DTDS [13divinyltetramethyl-disiloxane], and (c) DDTS [15divinyl33diphenyl1155tetramethyltrisiloxane].

(a)



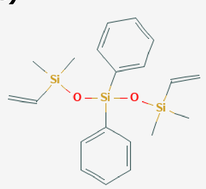
Molecular weight: 272.57 g/mol
Boiling Point: 198-200 °C

(b)



Molecular weight: 186.4 g/mol
Boiling Point: 139 °C

(c)



Molecular weight: 384.70 g/mol
Boiling Point: 141-144°C

Fig 1: Molecular structure of precursors (a) TPTS (b) DTDS (c) DDTS.

Method and Analysis Techniques

Method:

- Combine precursors with 1 wt% Dicumyl Peroxide (DCP - polymerizing agent)
- Crosslink in air at 180°C (oven)
- Crush crosslinked material into small pieces
- Pyrolyze at 800°C or 1200°C (furnace)

FTIR: FTIR is useful regarding the evolution of chemical bonding. Its peaks show the type and amount of bonds within a sample.

Raman: Raman spectroscopy is useful when analyzing pyrolyzed materials and is very sensitive/non-destructive towards carbon characterization.

TEM: TEM imaging provides highly magnified, high-resolution imaging.

EDX: EDX is a form of X-ray analysis which can provide insight regarding which elements a material is composed of.

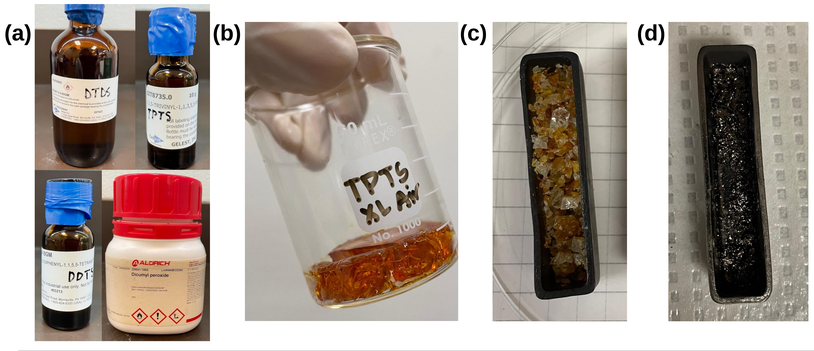


Fig 2: (a) DDTS, TPTS, DTDS precursors and DCP (b) crosslinked TPTS (c) TPTS after crosslinking (d) TPTS after pyrolyzing.

Data and Results

FTIR Analysis

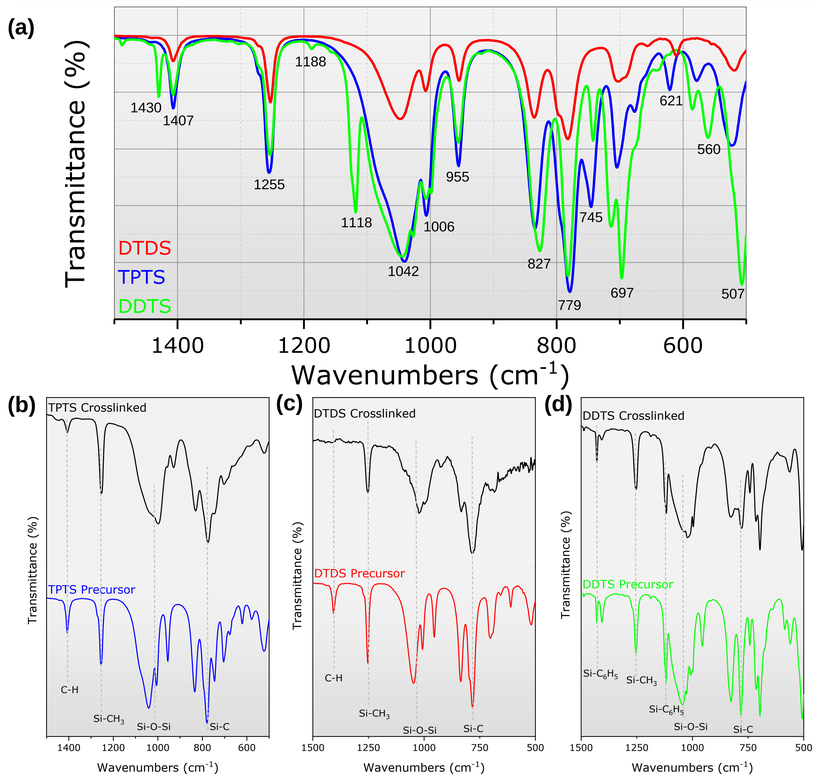


Fig 3: FTIR spectra of the precursor and crosslinked samples. Major peaks of crosslinked samples are labeled within the plot. (a) Comparison of chemical bonding between precursors (b) chemical bonding of TPTS (c) chemical bonding of DTDS (d) chemical bonding of DDTS.

Peaks in the crosslinked material show less intensity relative to the precursor as bonds are being broken. Reactions that could be occurring during crosslinking include decomposition reactions, such as dehydrogenation.

Raman Analysis

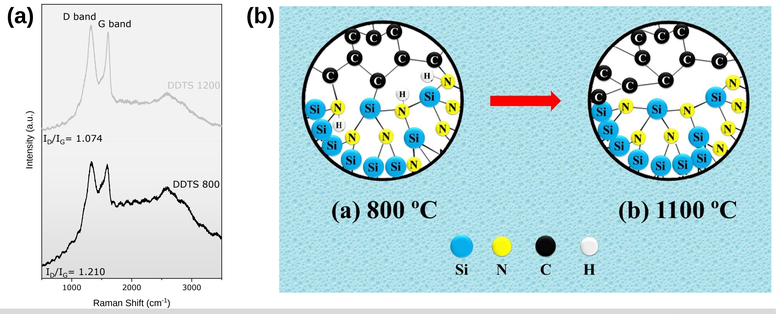


Fig 4: (a) Raman spectra of DDTS (b) independence of carbon phase[4]. Unclear peaks in 800°C indicates little formation of graphite, and more peaks under the ones shown. Clear peaks in 1200 °C indicate greater graphite formation. Decreasing peak ratio indicates more ordered carbon at higher temperatures.

TEM and EDX Analysis

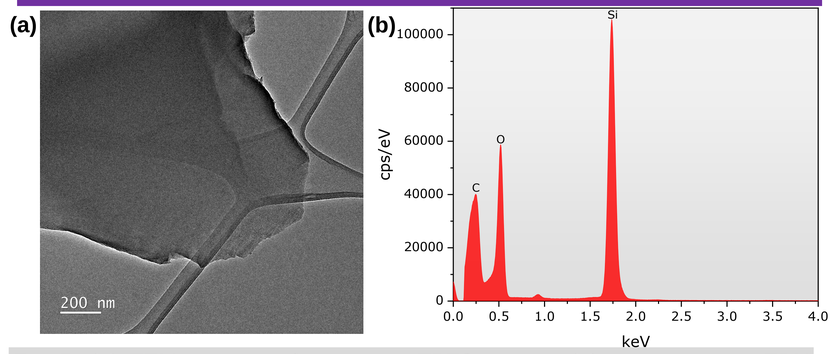


Fig 5: (a) TEM imaging of pyrolyzed TPTS particle (b) corresponding EDX spectra. Shows presence of elements Si, O, and C, as per expectation.

Yield Analysis

	TPTS	DTDS	DDTS
% Yield post crosslinking	59.31%	11.61%	67.12%
% Yield post pyrolysis	15.48%	3.59%	11.44%

The table above gives the yield of sample mass following both crosslinking and pyrolysis of all three precursors. DTDS showed the lowest yield following both processes, with a comparatively much lower molecular weight than the others. In general, crosslinking was followed by much mass loss. This mass loss could be due to fragmentation of the linear oligomer, followed by volatilization.

Conclusion and Future Work

This is a study which investigates the impact of the crosslinking mechanism and the carbon phase on the microstructure of polymer derived ceramics (PDCs). FTIR analysis confirmed the crosslinking mechanism as well as the initial molecular structure of the materials. Raman analysis confirmed the formation of the free carbon phase. Concerning yield, DTDS was seen to have the lowest yield by far as compared to the other precursors, likely due to its lower molecular weight. Further experimentation can be done to prevent mass loss, such as pyrolysis in an autoclave or use of better catalysts.

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References

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