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Sandia National Laboratories

LDRD LABORATORY DIRECTED **RESEARCH & DEVELOPMENT**

Thermally stable ceramics derived from borate-containing pre-ceramic polymers

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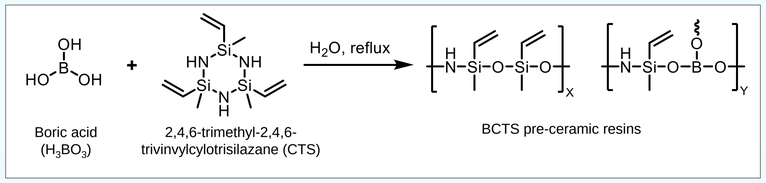
Introduction

Pre-ceramic polymers are macromolecules that yield ceramic products upon high-temperature pyrolysis.[1] These molecules are of interest due to synthetic tunability of the polymer backbone that modifies the resulting ceramic composition and physical properties. Furthermore, pre-ceramic polymers can be readily dissolved in solvents, making them ideal for application to substrates through various coating processes. Ceramic materials composed of SiBCN(O) elements are well-known for their robust stability and minimal outgassing at high temperatures, making them advantageous for applications as coatings in high-energy environments.

Within this project, we explored the synthesis of branched pre-ceramic polymers derived from boric acid and 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane (CTS) precursors with the aim of producing thermally-stable ceramic products with low outgassing. Pyrolysis of the resulting BCTS resins afforded black ceramics comprised of Si, O, and C in good yield. In addition, we chemically crosslinked the resins prior to pyrolysis to improve the final yield and ceramic shaping.



Boric acid (H_3BO_3) | 2,4,6-trimethyl-2,4,6-trivinylcylotrisilazane (CTS) | BCTS pre-ceramic resins

Figure 1. Synthetic scheme for preparation of BCTS pre-ceramic polymers.[2]

Methodology

- Synthesized reported BCTS pre-ceramic polymers by hydrolysis of CTS in the presence of H_3BO_3
- Varied the ratio of H_3BO_3 and CTS precursors in synthesis to tune properties pyrolyzed products
- Pyrolyzed bulk BCTS resins to characterize the elemental composition and thermal stability of resulting ceramics
- Performed thermal initiated crosslinking of free vinyl groups in BCTS resins prior to pyrolysis to improve ceramic yield and aid in substrate application

Results

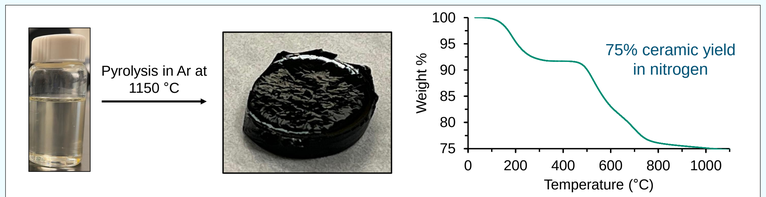
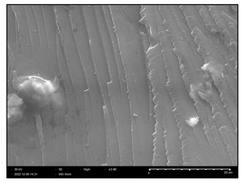


Figure 2. Pyrolysis and thermogravimetric analysis (TGA) of BCTS11 pre-ceramic polymer.

EDX data on BCTS11

Element	Mass [%]	Atom [%]	Rel. error [%]
Si	34.97	21.50	3.28
O	41.79	45.10	5.37
C	23.24	33.40	5.61
Sum	100.0	100.0	

SiOC composition determined by both EDX and LIBS analyses



Amorphous structure confirmed by pXRD

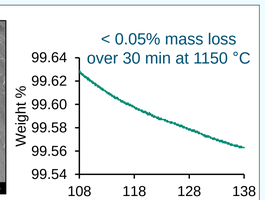
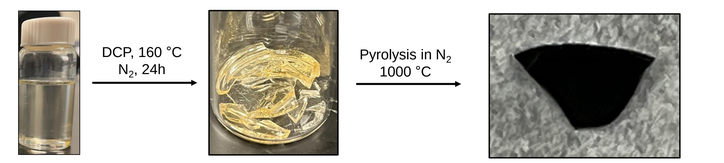


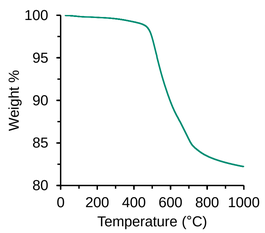
Figure 3. SEM, elemental analysis, and TGA data of BCTS11 ceramic.



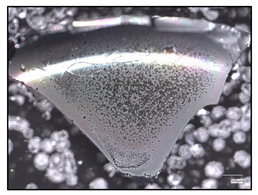
DCP thermal initiator used to crosslink free vinyl groups to form a rigid green body prior to pyrolysis

Final pyrolyzed ceramic maintained original shaping of starting green body

Figure 4. Crosslinking of BCTS11 resin prior to pyrolysis.



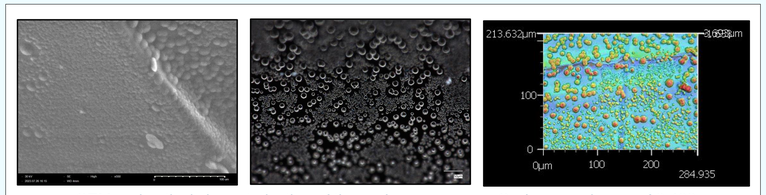
Crosslinking before pyrolysis improves ceramic yield by 7 %



BCTS11	Si	O	C
1	19.0%	55.8%	25.2%
2	16.5%	32.5%	51.0%
3	20.2%	27.1%	52.7%
4	27.6%	19.5%	52.9%
5	36.6%	--	63.4%
6	44.3%	--	55.7%
7	41.2%	--	58.8%
8	43.8%	--	56.2%
9	43.1%	--	56.9%
10	43.4%	--	56.6%

Drilling LIBS analysis shows SiC interior

Figure 5. TGA and LIBS analysis of crosslinked BCTS11 ceramic.



SEM and optical characterization of the surface reveals spherical morphology

Surface roughness of 0.408 µm

Figure 6. Surface characterization of crosslinked BCTS11 ceramic.

Conclusions and Outlook

- Pyrolysis of BCTS pre-ceramic polymers yields amorphous ceramic materials comprised of Si, O, and C with moderate ceramic yield
- Chemically crosslinking the free vinyl groups in the resins prior to pyrolysis forms a rigid green body that improves ceramic yield
- Surface analysis reveals spherical morphology on the surface
- Application to stainless steel substrates
- Determination of mass loss and outgassing at high temperatures

Acknowledgements

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References

[1] Ackley, B; Martin, K; Key, Thomas; Clarkson, C; Bowen, J; Posey, N; Ponder, P; Apostolov, Z; Cinibulk, M; Pruyn, T, and Dickerson, M; *Chem. Rev.* **2023**, 123, 4188 – 4236

[2] Thiyagarajan, G; and Devasia, R; *J. Am. Ceram. Soc.* **2019**, 102, 476 – 489

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