

# MOLECULAR DESIGN OF PRECURSORS AND APPLICATION IN CMCs PREPARATION

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**SUMMARY:** In order to satisfy the requirements for preceramic polymers (low viscosity, crosslinkability, and high ceramic yield) aiming to prepare ceramic matrix composites, a series of silazane oligomers were firstly molecularly designed, then synthesized, characterized, and pyrolyzed to obtain ceramic yields. One of the precursors was used to prepare carbon fiber three dimensional braided preform reinforced composite, and maximum flexural strength 425.3MPa and flexural toughness over 11.5MPa·m<sup>1/2</sup> were achieved.

**KEYWORDS:** Molecular Design, Preceramic Polymer, CMCs Preparation

## INTRODUCTION

Since the successful applications of organosilicon precursors in manufacturing ceramic fibers (e.g., Nicalon and Tyranno fiber)[1, 2, 3], this route is gaining attention in preparing Ceramic Matrix Composites (CMCs) for its unique plastic forming ability. Combined with weave technology (fiber architecture), such a polymer forming-pyrolysis process shows great potential to realize near-net-shaping of Continuous Fiber-reinforced CMCs (CFCMCs), especially with complicated and large scale structures.

Many papers have concerned about this process [4, 5, 6]. Polycarbosilane (PCS) and polysilazane (PSZ) are commonly used as precursors to form ceramic matrices. These precursors, originally used for fiber preparation, have some characteristics unsuitable for CFCMCs preparation. PCS usually leads to ~60wt% ceramic yield upon pyrolysis, and easily foams [7], so ten cycles of infiltration-pyrolysis are usually required to obtain a relatively dense composite.

Taking account of the requirements in the process, the precursors for CFCMCs must have two basic characteristics: low viscosity (either as solution or as melt) and good wettability with fibers to benefit infiltration, and high ceramic yield to decrease infiltration-pyrolysis cycles. These characteristics can only be met through molecular design, that is, the precursors must be oligomers with low molecular weights, and have latent active groups to render further crosslinking to enhance ceramic yield. Chong and his coworkers [8] reported one silazane with good processability and high ceramic yield (over 80wt% up to 1273K), and Interrante et al. [9] patented one kind of carbosilanes with Si-H, C=C and/or CH<sub>2</sub>=CHCH<sub>2</sub> groups in the molecules, though both are time-consuming and cost-expensive via multiple steps.

In the present paper a series of precursors with latent functionalities were designed, synthesized, and used to prepare CMCs.

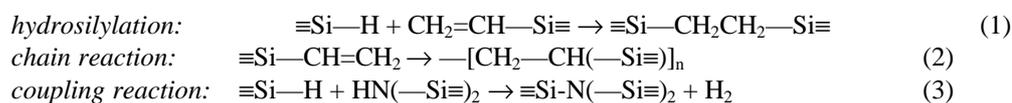
## Principles of molecular design

There are many active groups (either silicon, or carbon, or nitrogen functional) can be introduced into the precursors, but reasonable ones must comply with the following criteria:

*a.* In the crosslinking reactions, chain reactions are preferred to condensation polymerization, simply because the release of gases or low molecules in condensation will destroy the shape and cause pores in the bulk.

*b.* The agents are conveniently available and cheap. Thus, multiple steps of agent synthesis is not acceptable.

We considered three groups (Si-H, C=C, and N-H) as latent functionalities. Possible reactions between these groups are as follows:



## RESULTS AND DISCUSSION

### Properties of Precursors

Eight active group-containing precursors are prepared and characterized, as details are listed in Table 1.

Table 1: Properties of synthesized products

Product	Agents <sup>1</sup>	structure and/or formula	appearance	Crosslinking	yield <sup>3</sup>
HVASZ	H+V+NH <sub>3</sub>	[MeHSiNH] <sub>m</sub> [MeViSiNH] <sub>n</sub>	liquid	H <sub>2</sub> PtCl <sub>6</sub> and DCP	73.4%
HAASZ	H+A-NH <sub>2</sub>	[MeHSiN(CH <sub>2</sub> -CH=CH <sub>2</sub> ) <sub>4</sub> ]	liquid	H <sub>2</sub> PtCl <sub>6</sub> and DCP	71.0%
MAASZ	M+A-NH <sub>2</sub>	[Me <sub>2</sub> SiN(CH <sub>2</sub> -CH=CH <sub>2</sub> ) <sub>4</sub> ]	liquid	DCP <sup>2</sup>	65.4%
HVHSZ	H+V+N <sub>2</sub> H <sub>4</sub>	[MeHSiN <sub>2</sub> H <sub>2</sub> ] <sub>x</sub> [MeViSiN <sub>2</sub> H <sub>2</sub> ] <sub>y</sub>	liquid	H <sub>2</sub> PtCl <sub>6</sub> and DCP	75.1%
HCSZ	H+Ag <sub>2</sub> CN <sub>2</sub>	[MeHSiNCN] <sub>x</sub>	solid	Heat	73.5%
VCS	V+Ag <sub>2</sub> CN <sub>2</sub>	[MeViSiNCN] <sub>x</sub>	liquid	DCP	64.4%
VTSZ	V+T+NH <sub>3</sub>	[MeViSiNH] <sub>x</sub> [MeSi(NH) <sub>3/2</sub> ] <sub>y</sub>	liquid	DCP	66.4%
HTSZ	H+T+NH <sub>3</sub>	[MeHSiNH] <sub>x</sub> [MeSi(NH) <sub>3/2</sub> ] <sub>y</sub>	solid/liquid	heat	80.1%

Note: 1. H, V, M, T and A-NH<sub>2</sub> indicate MeHSiCl<sub>2</sub>, Me(CH<sub>2</sub>=CH)SiCl<sub>2</sub>, Me<sub>2</sub>SiCl<sub>2</sub>, MeSiCl<sub>3</sub>, and CH<sub>2</sub>=CH-CH<sub>2</sub>NH<sub>2</sub>, respectively. 2. DCP indicate dicumyl peroxide. 3. Pyrolytic condition: ramp rate 2K/min, maximum temperature 1273K, N<sub>2</sub>.

As is expected, six products are liquid with low viscosity, satisfying the requirement for infiltration. One is solid, and foams when heated up to 770K. Crosslinking treatment shows that hydrosilylation reactions always occur in the presence of both C=C and Si-H groups, and chain reaction via C=C is also effective to cause crosslinking.

Ceramic yields in Table 1 appear, in general, that high yield goes with unfavorable processability. MAASZ has the least viscosity, and thus the lowest ceramic yield in the same pyrolysis condition. Further study shows ceramic yield is largely determined by crosslinking

method (which determines crosslinking depth) and pyrolysis condition, as is clearly proved in Table 2.

Table 2: Ceramic yields under different conditions (HVASZ, wt%)

pyrolysis	catalyst (initiator)	ramping rate (K/min)	yield (1273K)
TG	none	10	57.6
TG	DCP	10	64.9
TG	H <sub>2</sub> PtCl <sub>6</sub>	10	70.0
TG	DCP	5	67.2
TG	H <sub>2</sub> PtCl <sub>6</sub>	5	71.6
tube furnace	H <sub>2</sub> PtCl <sub>6</sub>	1	74.0
tube furnace	H <sub>2</sub> PtCl <sub>6</sub>	0.3	78.5

### Preparation of Carbon Fiber Three Dimensional Braided Preform (3D-B C<sub>f</sub>) Reinforced Ceramic Matrix Composites

One of the precursors, HVASZ, with excellent processibility and high ceramic yield, was chosen to prepare 3D-B C<sub>f</sub> reinforced ceramic matrix composites. The processing scheme has been described elsewhere [10]. The properties of the composite, after eight cycles of infiltration-crosslinking-pyrolysis, were listed in Table 3. Load-strain curve and surface appearance of fractured specimens indicate a tough destroy.

Table 3: Properties of 3D-B C<sub>f</sub>/Si-C-N composites

Specimen No.	$\rho$ (g/cm <sup>3</sup> )	$\sigma_f$ (Mpa)	E (Gpa)	K <sub>IC</sub> (MPa·m <sup>1/2</sup> )
1	1.67	368.3	53.4	14.57
2	1.68	425.3	64.6	11.55
3	1.61	313.8	50.9	15.20
4	1.60	289.3	45.6	18.87
5	1.61	305.4	52.1	13.60
6	1.58	297.5	53.4	16.47

## CONCLUSIONS

1. A series of preceramic oligomers with active groups were designed, synthesized, and pyrolyzed to obtain ceramic yield. Crosslinking process were investigated in detail to obtain highly crosslinked polymers, and thus high ceramic yield.
2. One of the precursors was chosen to prepared carbon fiber three dimensional braided preform reinforced composite. Maximum flexural strength of 425.3MPa and flexural toughness of over 11.5MPa·m<sup>1/2</sup> were achieved.

## REFERENCES

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1. Yajima S., Okamura K., Hayashi J. and Omori M., "Synthesis of Continuous SiC Fibers with High Tensile Strength", *Journal of American Ceramic Society*, Vol.59, No.7-8, 1975, pp. 324-327
2. Yajima S., Hayashi J., and Omori M., "Continuous Silicon Carbide Fiber of High Tensile Strength", *Chemistry Letters*, 1975, Vol.9, pp.931-34
3. Yajima S., "Special Heat-Resisting Materials from Organometallic Polymers", *Ceramic Bulletin*, 1983, Vol.62, No.8, pp.893-915
4. Nakano K., Kamiya A., Nishino Y., Imura T. and Chou T.-W., "Fabrication and Characterization of Three Dimensional Carbon Fiber Reinforced Silicon Carbide and Silicon Nitride Composites", *Journal of American Ceramic Society*, Vol.78, No.10, 1995, pp. 2811-2814
5. Sato K., Suzuki T., Funayama O. and Isoda T., "Fabrication of Silicon Nitride Based Composites by Impregnation with Perhydrodopolysilazane", *Journal of Ceramic Society of Japan*, Vol.100, No.4, 1992, pp. 444-447.
6. Riccitiello S., Marshall M., "3-D Ceramic Matrix Composite Development", *Journal of Advanced Materials*, Vol.1, 1994, pp.22-28
7. Su B., Chen Z., Wu X., Wang X., "Crosslinking Study of Polycarbosilane/Divinyl Benzene", *Gaojishu Tongxun (High Technology Letters)*, Vol.6, 1993, pp.78-82 (Chinese)
8. Chong Kwet Yive N.S., Corriu R., Leclercq D., Mutin P.-H. And Vioux A., "Polyvinylsilazane: A Novel Precursor to Silicon Carbonitride", *New Journal of Chemistry*, Vol.15, 1991, pp.85-92.
9. Whitmarsh C.K. and Interrante L.V., "Carbosilane Polymer Precursors to Silicon Carbide Ceramics", U.S. Patent 5,153,295, Oct.6, 1992
10. Hu H., Chen Z., Feng C., Zhang C., and Song Y., "Three-Dimensional Braided Preform Reinforced Si-C-N Composites Prepared by Precursor Pyrolysis", *Journal of Material Science Letters*, Vol.17, 1998, pp73-74