

# Silsesquioxanes as Precursors to Ceramic Composites

(NASA-TM-89893) SILSESQUIOXANES AS  
PRECURSORS TO CERAMIC COMPOSITES (NASA) 16  
p Avail: NTIS HC A02/MF A01 CSCL 11D

N87-25432

G3/24 Unclass  
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Prepared for the  
11th Annual Conference on Composites, Advanced Ceramics,  
and Composite Materials  
cosponsored by the American Ceramic Society, DOD, and NASA  
Cocoa Beach, Florida, January 18-23, 1987



# SILSESQUOXANES AS PRECURSORS TO CERAMIC COMPOSITES

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## SUMMARY

Silsesquioxanes having the general structure  $\text{RSiO}_{1.5}$ , where R = methyl, propyl, or phenyl, melt flow at 70 to 100 °C. Above 100 °C, free -OH groups condense. At 225 °C further crosslinking occurs, and the materials form thermosets. Pyrolysis, with accompanying loss of volatiles, takes place at nominally 525 °C. At higher temperatures, the R group serves as an internal carbon source for carbothermal reduction to SiC accompanied by the evolution of CO. By blending silsesquioxanes with varying R groups, both the melt rheology and composition of the fired ceramic can be controlled. Fibers can be spun from the melt which are stable in argon to 1400 °C. The silsesquioxanes also have been used as matrix precursors for Nicalon and  $\alpha$ -SiC platelet reinforced composites.

## INTRODUCTION

Utilization of polymeric precursors to ceramic fibers and ceramic matrix composites offers ease of processing at low temperatures, and the opportunity to produce small diameter, continuous fibers and complex-shaped, flaw tolerant, ceramic composite parts.

Polysilsesquioxane gels having the general formula  $(\text{RSiO}_{1.5})_n$  have been used to produce SiC powders (refs. 1 and 2). Since the carbon is covalently bonded to the silicon, the ratio of C/Si in the starting material, the extent

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of crosslinking and the pyrolysis conditions determine the yield and properties of the resulting powders.

Proposed polysilsesquioxane structures are shown in figure 1. It is presumed that the unordered structure is the more common, but that lower molecular weight molecules, particularly those with  $R = \text{phenyl}$ , may adopt the ladder conformation (ref. 3). The nature of the  $R$  group and molecular structure of the gel also influence the rheological behavior of the silsesquioxanes. Hence, by modifying the starting composition and crosslinked structure, and by forming copolymers, conditions suitable for processing both small diameter fibers and forming composite matrices can be determined.

The composition of the final ceramic will be determined by the stoichiometry of the polymer or copolymer, which may undergo several reactions prior to reaching a temperature at which carbothermal reduction can occur. Ideally, a  $C/Si$  ratio of 5/2 at the onset of the carbothermal reduction should yield stoichiometric  $SiC$ . However, deviations from this ratio would be expected to produce other products, including excess carbon,  $SiO_2$ , and  $SiO$  in route to the final ceramic (fig. 2).

This work focuses on demonstrating the feasibility of silsesquioxanes as potential precursors to both small diameter fibers and ceramic matrices for continuous fiber composites.

The  $R$  groups of the polymers studied included methyl, propyl, phenyl, and vinyl, as well as copolymers of these. Composites reinforced with Nicalon fiber were fabricated and characterized by optical microscopy, scanning electron microscopy (SEM), TGA, differential thermal analysis (DTA), and dilatometry (TMA). Fibers were studied by SEM.

Experimental polymethyl-, polyphenylpropyl-, polyphenyl-, and polyphenylvinylsilsequioxanes were purchased from Petrarch Systems, Bristol, PA. Nicalon fiber, a product of Nippon Carbon, Tokyo, was obtained from Dow Corning, Midland, MI. The  $SiC$  platelets are a product of American Matrix, Inc., Knoxville, TN.

The polysilsesquioxanes were characterized by thermogravimetric analysis (TGA), microdielectrometry, Fourier transform infrared (FTIR) spectroscopy, and physical observation. TGA studies were carried out at several heating rates using a Perkin-Elmer TGS-2 on both as-received samples and Nicalon/silsesquioxane composites.

Dielectric monitoring was conducted using a Micromet Eumetric System II. Polysilsesquioxane powders were melted onto the dielectric sensor to obtain good wetting, and the sensor and sample then heated in a DSC cell. Measurements were obtained simultaneously at 1, 10, 100, 1000, and 10 000 Hz. FTIR spectra were obtained on films cast from tetrahydrofuran onto KBr discs using a Perkin Elmer 1700 spectrophotometer with double precision software at a resolution of  $4\text{ cm}^{-1}$ . Films held between two KBr discs were heated in-situ and the spectra ratioed to KBr at the same temperature.

Fibers were hand drawn from the polysilsesquioxane melt maintained at a temperature of 120 to 130 °C. They were then exposed to ultraviolet light at

254 nm and a power density of 12 to 15 mW/cm<sup>2</sup> for periods of 2 to 25 hr. Irradiated fibers were heated from 0 to 225 °C at 3 °C/min, and held at 225 °C for 3 hr. The temperature then was increased at 3 °C/min to 1000, 1200, or 1400 °C. Fibers were heated in an argon or nitrogen atmosphere, and characterized by scanning electron microscopy (SEM).

Composites were fabricated by winding Nicalon fiber at 14 turns/cm on a mandrel, and coating the fiber with the polysilsesquioxane melt at a temperature of nominally 150 °C. A commercial silicone glycol surfactant, Dow Corning A57, was added to some resin batches to increase flow. Addition of A57 was at a ratio of 3.75 ml additive per 50 gm of polysilsesquioxane powder. The prepreg was removed from the mandrel, cut and stacked 10 plies high in a matched metal die mold. The mold was inserted into a cold press. Contact pressure was applied and press temperature was increased to 150 °C; these conditions were maintained for 3 hr. The temperature was increased to 225 °C, 689 Pa pressure applied, and temperature and pressure maintained for 90 min. Composites were pyrolyzed in air at 525 °C for 2 hr. Pyrolyzed composites were heated at 3 °C/min to 1000, 1200 or 1400 °C in flowing argon.

Platelet reinforced composites were formed by mixing the platelets with the dry ground polysilsesquioxane powders and hot pressing. Platelets were added at a ratio of 7.88 gm per 6.24 gm powder, nominally 50 vol %.

Composites were characterized by optical microscopy, SEM and energy dispersive spectroscopy (EDS), wavelength dispersive spectroscopy (WDS), and thermal expansion.

## RESULTS AND DISCUSSION

### Polysilsesquioxanes

Four polysilsesquioxanes were screened initially: polymethyl-, polyphenylpropyl-, polyphenyl-, and polyphenylvinylsilsesquioxane. Of these, the polymethyl and polyphenylpropyl exhibited superior rheological behavior; these were studied both individually and as copolymer blends. The as-received phenylpropyl copolymer contains seven phenyl groups to three propyl, and was blended with the methyl polymer to produce an initial C/Si ratio of nominally 5/2, denoted as Batch 2. The Batch 1 material contained a slightly higher initial concentration of phenyl groups.

Weight change as a function of temperature for both batches obtained at a heating rate of 5 °C/min in nitrogen is shown in figure 3. Between ambient temperature and 1000 °C weight transitions are observed at approximately 200 and 525 °C, with a possible third, smaller change at nominally 750 °C. The first of these is more pronounced for the higher methyl composition.

Infrared spectra of thin films heated between KBr discs were obtained to characterize the lower temperature region (23 to 235 °C). The FTIR spectra of polyphenylpropylsilsesquioxane are shown in figure 4. The as-received materials exhibit an H-bonded OH stretch between 3600 and 3200 cm<sup>-1</sup>, as well as a silanol peak at 943 to 835 cm<sup>-1</sup>, which both disappear on heating to 150 °C. The Si-O-Si peak in the 1240 to 955 cm<sup>-1</sup> region, comprised of several overlapping bands, exhibits an overall increase in intensity, with more substantial



increases at 1106 and 1035  $\text{cm}^{-1}$ , possibly characteristic of the development of a more ordered, ladder polymer. The spectral behavior of polymethylsilsesquioxane was similar to the phenylpropyl. The spectra of polyphenylsilsesquioxane, by comparison (fig. 5), has a distinct band at 1035  $\text{cm}^{-1}$ , probably characteristic of a greater degree of ladder polymer, and shows only minor changes in band shape on heating to 235 °C. No residual silanol groups were observed.

Comparisons of figures 3 and 4 show that the silanol condensation does not contribute significantly to any weight change, while the TGA transition at 200 °C is accompanied by changes in the Si-O-Si structure.

Monitoring resistivity (conductivity<sup>-1</sup>) (ref. 4) (fig. 6) for the mixed polysilsesquioxanes (Batch 2) shows that as the temperature is increased from ambient to 225 °C, then held at 225 °C for 2 hr, the resistivity initially decreases with temperature, corresponding to a decrease in viscosity, then increases as the polymer cures, undergoing a thermoset type of crosslinking. (At this stage the polymer does not remelt.) An expanded plot of the initial 30 min of the reaction is shown in figure 7. The physical observation of boiling of the polymer blend at 180 °C corresponds to the onset of the first TGA transition (fig. 3). The point on the curve labelled "flow" corresponds to a viscosity empirically found suitable for fiber impregnation, while that indicated as "fibers" was appropriate for fiber formation.

### Fibers

Fibers 30 to 40  $\mu\text{m}$  in diameter were hand drawn from the polysilsesquioxane melt in lengths from 4 to 8 ft, at a temperature of 120 to 130 °C. As drawn fibers will remelt on further heating, the polysilsesquioxanes crosslink on uv irradiation at 254 nm; however, the extinction coefficient is high, so that crosslinking occurs on the surface and not throughout the bulk of the fiber.

Fibers irradiated for 3 and 25 hr are shown in figure 8. Following uv exposure, the tip of the fiber was touched against a hot plate, remelting the noncrosslinked bulk polymer, and revealing a crosslinked shell which does not melt. At 3 hr (fig. 8(a)) this shell is quite thin (<2  $\mu\text{m}$ ). As exposure time is increased, this crosslinked material shrinks relative to the bulk of the fiber, splitting the fiber (fig. 8(b)). Hence, the entire fiber cannot be crosslinked by uv irradiation. However, once even a thin crosslinked shell has been formed, the fiber can be heated to 225 °C and the fiber bulk crosslinked thermally, as shown by the dielectric changes in the polymer which occur at this temperature (fig. 6). Once the bulk of the fiber has undergone crosslinking, the fibers can be heated further without losing their shape. Fibers heated to 1000, 1200, and 1400 °C in argon and fractured by hand are shown in figure 9. Uv exposure was decreased to as little as 2 hr in some cases without affecting the fibers' ability to survive to high temperatures.

### Composites

Nicalon/silsesquioxane composites are shown as hot pressed in figure 10. The resin exhibits good flow into the fiber tow, producing few voids. Thermal expansion measurements made as the hot pressed composite is heated further

(fig. 11) show a region of rapid expansion between 100 to 200 °C. As the polymer matrix begins to cure, the expansion, while still positive, decreases in slope. Above 460 °C, as pyrolysis occurs, the composite shrinks, corresponding to the onset of weight loss. In unidirectional composites this shrinkage is accompanied by the formation of matrix cracks (fig. 12). Platelet reinforced composites did not exhibit the surface cracking observed for the Nicalon reinforced material. They did not undergo dimensional changes on pyrolysis, but developed more uniformly distributed matrix porosity (fig. 13).

Composites which were pyrolyzed at 525 °C were subsequently heated at 3 °C/min in argon to 1000, 1200, or 1400 °C, then fractured at room temperature in three point bending at a span to depth ratio of 32:1. Fracture surfaces are shown in figure 14. In the sample heated to 1000 °C (fig. 14(a)), fiber pullout is observed on the tensile surface, as is a shear failure at midplane. After heating to 1200 °C (fig. 14(b)), failure of fiber bundles, rather than individual fiber pullout, predominates. In the sample heated to 1400 °C (fig. 14(c)), reaction between the fiber and the matrix appears to have occurred. The tensile and compressive surfaces are not readily distinguishable, and the fracture is characteristic of brittle failure.

A piece of the Nicalon/silsesquioxane composite which had been heated to 1200 °C in argon was vacuum infiltrated with epoxy, polished, and examined by EDS to map silicon and WDS to map carbon and oxygen. Results are shown in figure 15. The bright areas on the carbon map correspond to epoxy. Comparison of the matrix with the Nicalon fibers shows that the carbon content of both is comparable. The silicon content of the fibers is slightly greater than that of the matrix, while the oxygen content is slightly lower.

## CONCLUSIONS

Polysilsesquioxanes show potential as precursors to both small diameter fibers and ceramic matrices. Modification of the polysilsesquioxane structure provides a means of controlling both the melt rheology and stoichiometry of the ceramic product. Low temperature processibility of both fibers and composites has been demonstrated.

Matrix cracking and shrinkage observed in unidirectional composites reinforced with Nicalon suggests the need to explore two- and three-dimensional weaves as opposed to crossply composite layup. Platelet reinforcement has demonstrated that large scale matrix cracking can be minimized or eliminated in favor of more uniformly distributed matrix porosity.

## ACKNOWLEDGMENTS

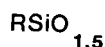
The authors wish to thank Dave Hull, Ron Phillips, and Earl Hanes for their contributions to this work.

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#### SILSESQUIOXANES



R = methyl, propyl, vinyl, phenyl

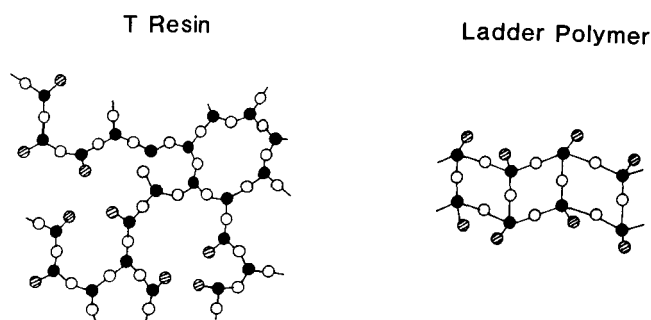


FIGURE 1. - STRUCTURE OF POLYSILSESQUIOXANES.

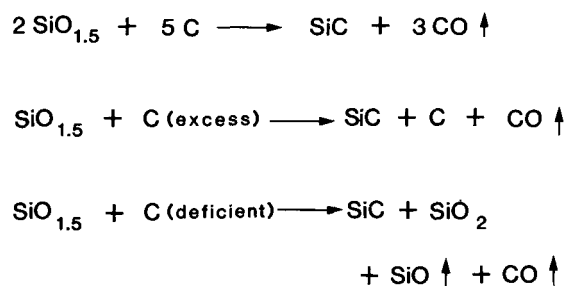


FIGURE 2. - POSSIBLE CARBOTHERMAL REDUCTION REACTIONS.

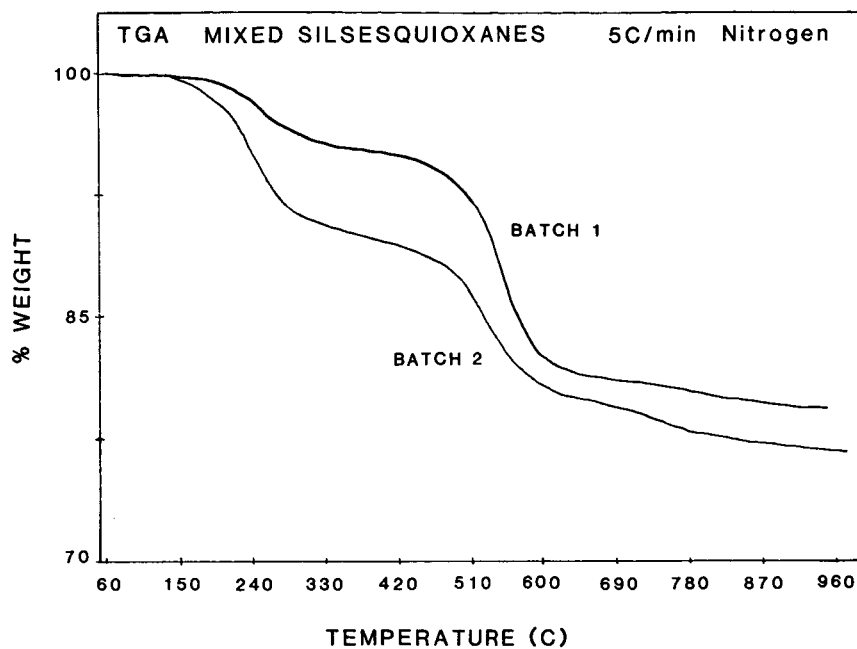


FIGURE 3. - TGA OF MIXED POLYSILSESQUIOXANES OBTAINED AT 5 °C/MIN IN NITROGEN.

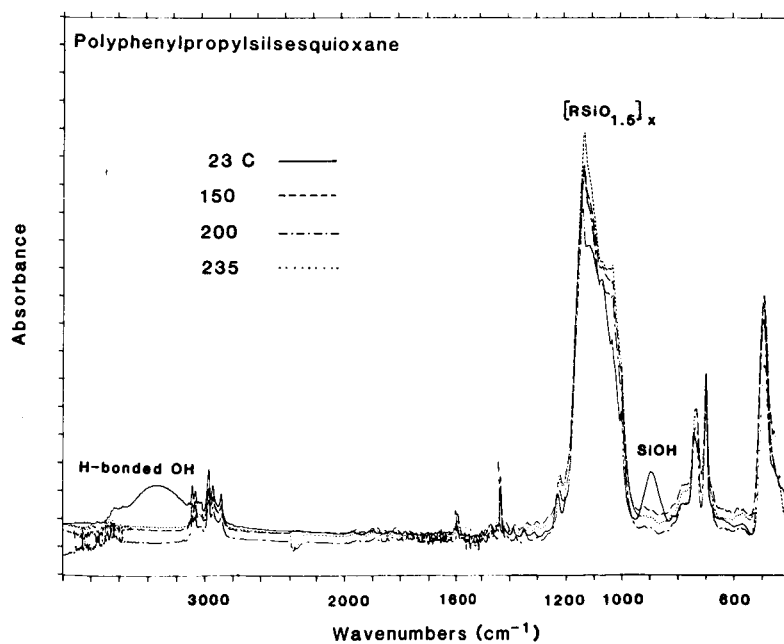


FIGURE 4. - FTIR SPECTRA OF POLYPHENYLPROPYLSILSESQUIOXANE.

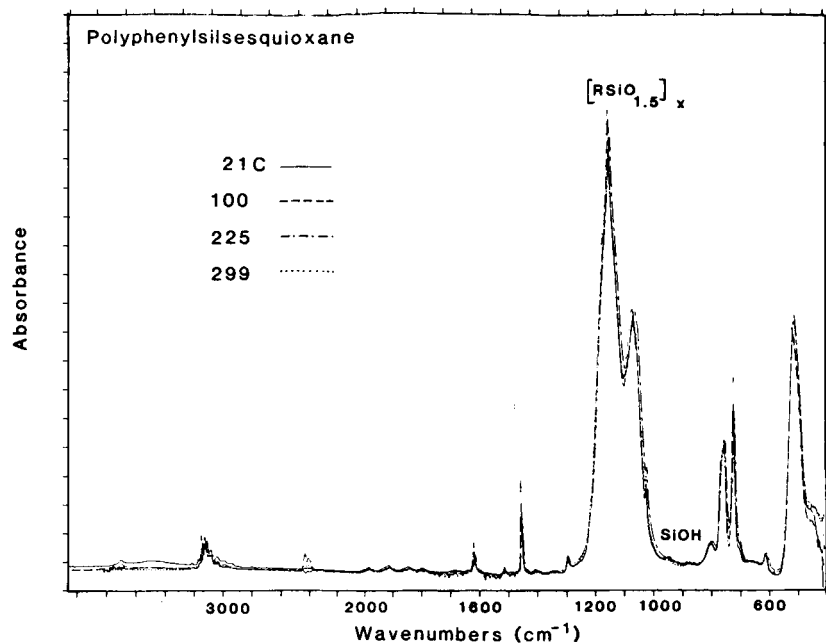


FIGURE 5. - FTIR SPECTRA OF POLYPHENYLSILSESQUIOXANE.

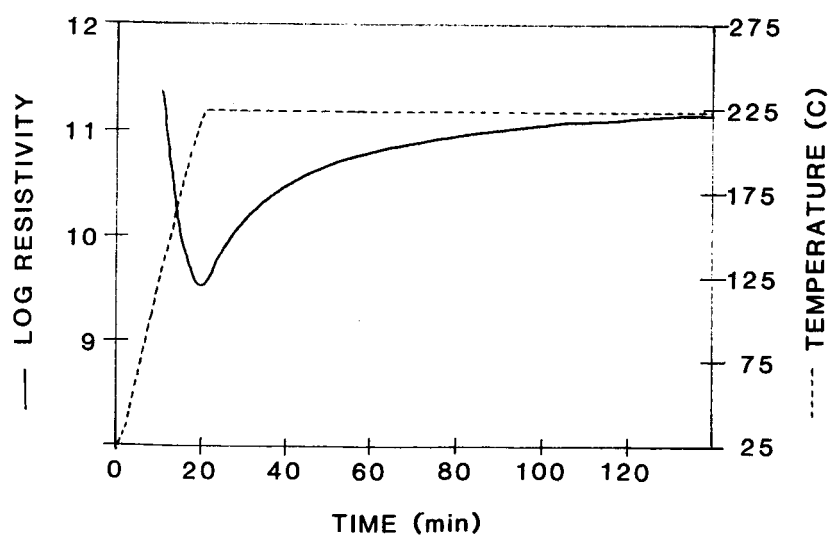


FIGURE 6. - RESISTIVITY OF MIXED POLYSILSESQUIOXANES AS TEMPERATURE IS INCREASED TO 225 °C AND HELD FOR 2 HR.

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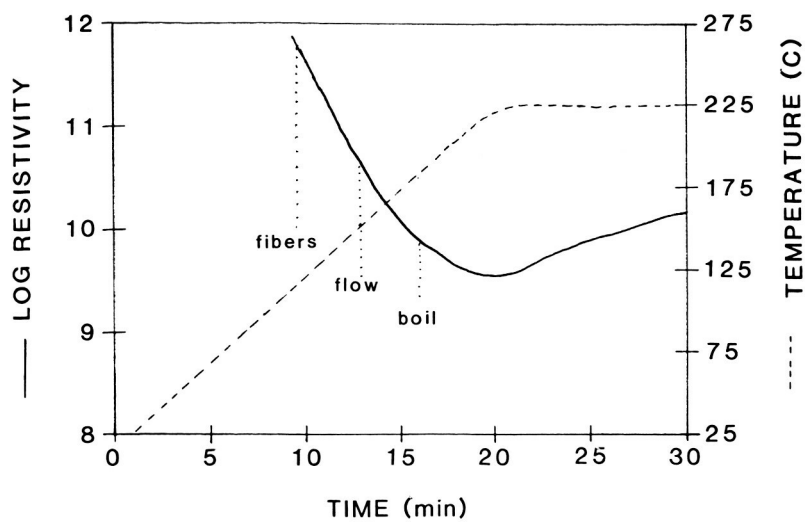


FIGURE 7. - RESISTIVITY OF MIXED POLYSILSESIQUOXANES DURING INITIAL 30 MIN OF CURE.

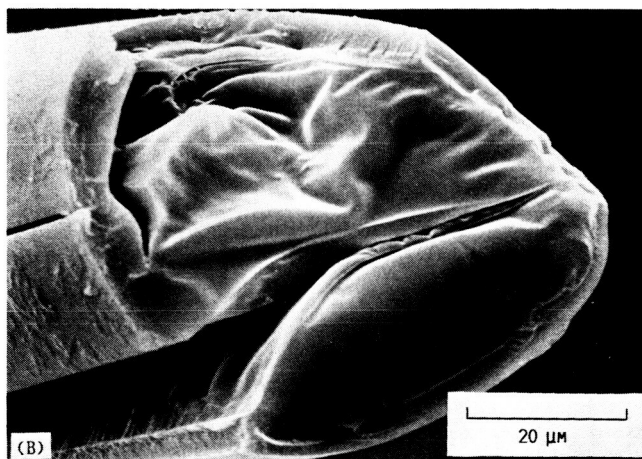
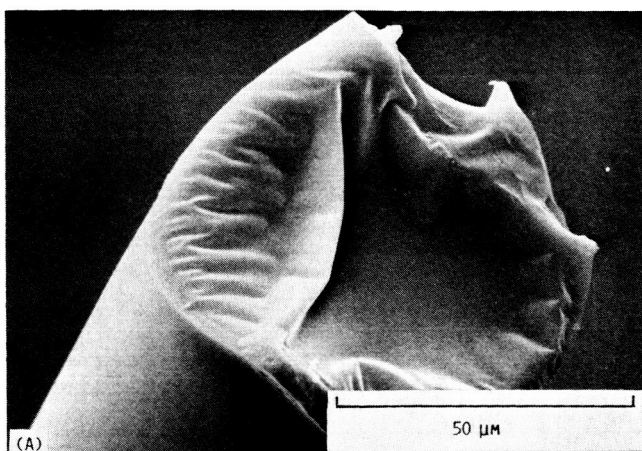


FIGURE 8. - POLYSILSESIQUOXANE FIBERS FOLLOWING UV EXPOSURE AT 254 NM FOR (A) 3 AND (B) 25 HR.

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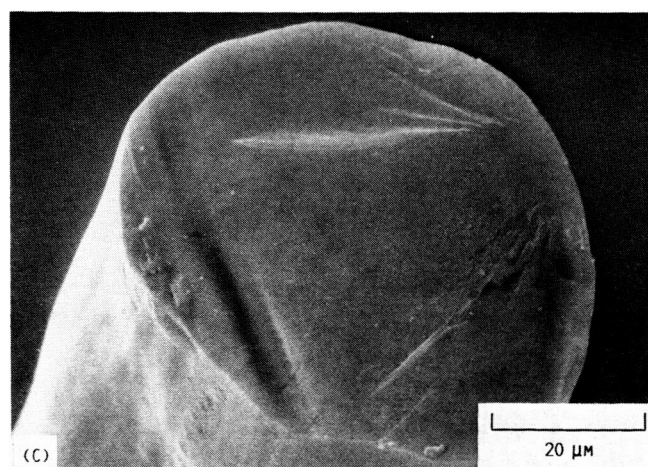
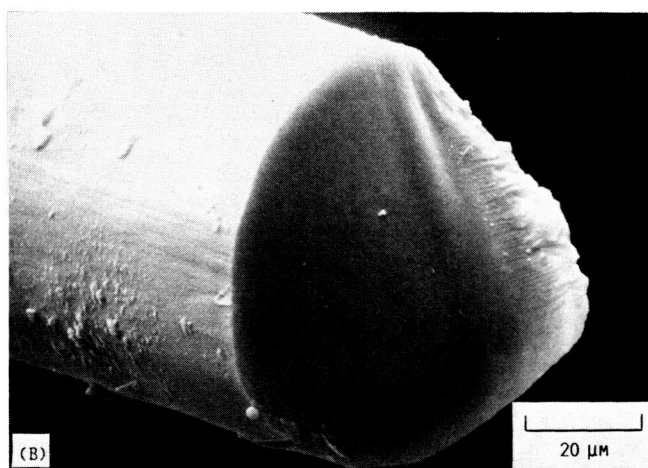
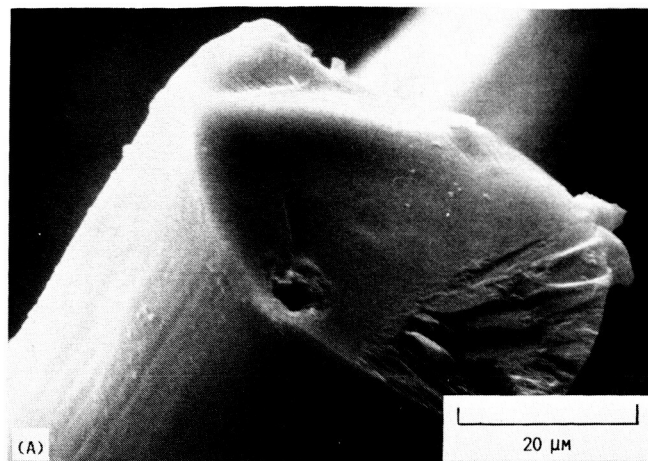


FIGURE 9. - POLYSILSESQUOXANE FIBERS HEATED IN ARGON TO (A) 1000, (B) 1200, AND (C) 1400 °C.

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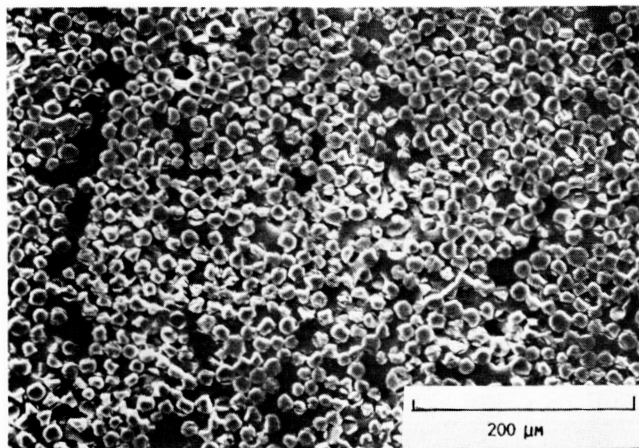


FIGURE 10. - AS HOT-PRESSED NICALON/SILSESQUIOXANE COMPOSITE.

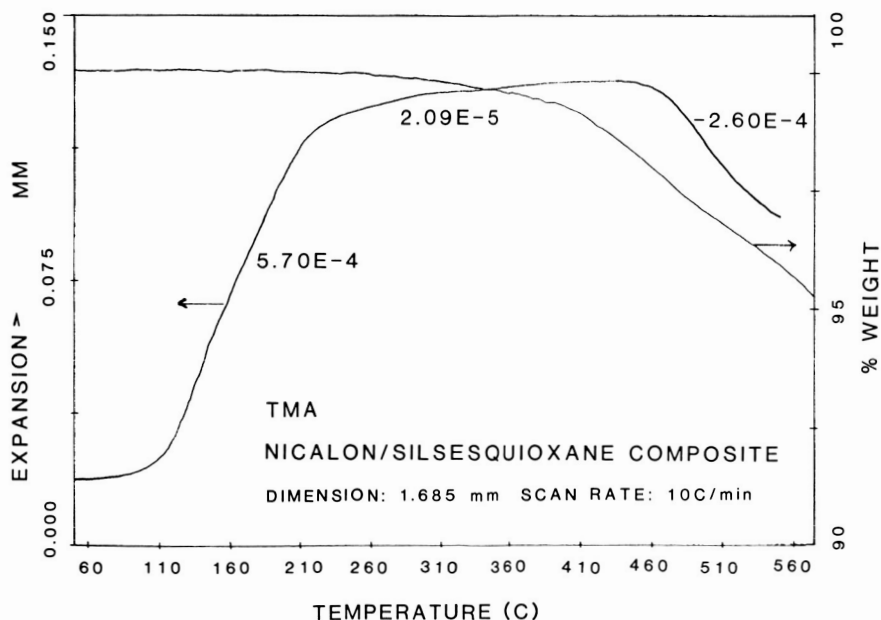


FIGURE 11. - THERMAL EXPANSION OF A NICALON/SILSESQUIOXANE COMPOSITE MEASURED THROUGH THE THICKNESS OF THE COMPOSITE. COEFFICIENTS OF EXPANSION ARE INDICATED FOR EACH REGION. WEIGHT CHANGE OF THE COMPOSITE WITH TEMPERATURE IS SUPERIMPOSED FOR COMPARISON.



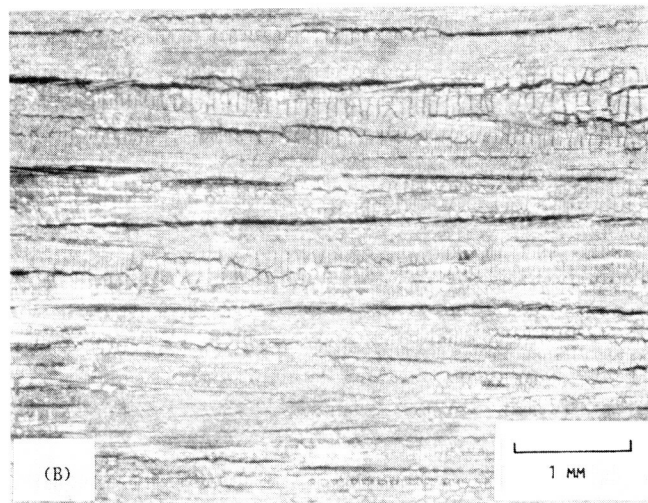
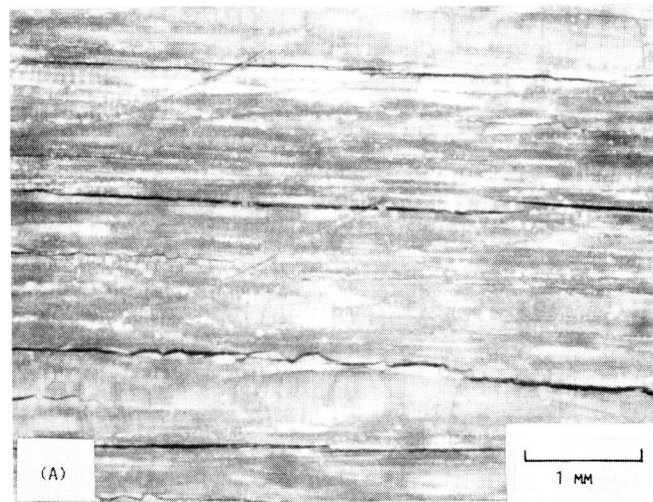


FIGURE 12. - COMPOSITE SURFACES OF NICALON/SILSEQUIOXANE COMPOSITES  
(A) AFTER PYROLYSIS AT 525 °C FOR 2 HR AND (B) FOLLOWING SUBSE-  
QUENT HEATING TO 1000 °C.

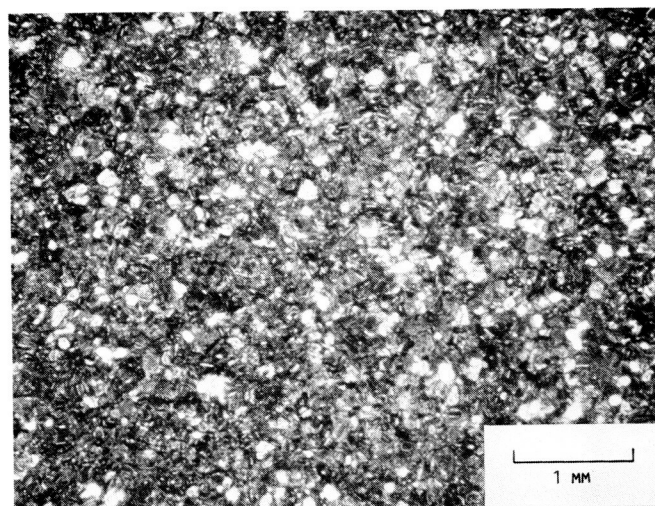


FIGURE 13. - PLATELET REINFORCED SILSEQUIOXANE COMPOSITE HEATED  
TO 1000 °C.

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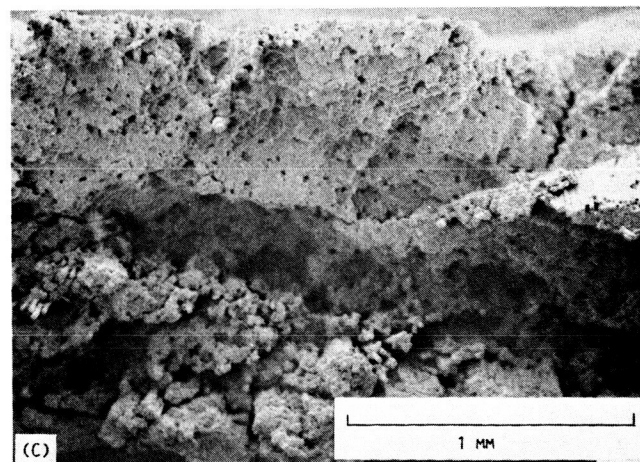
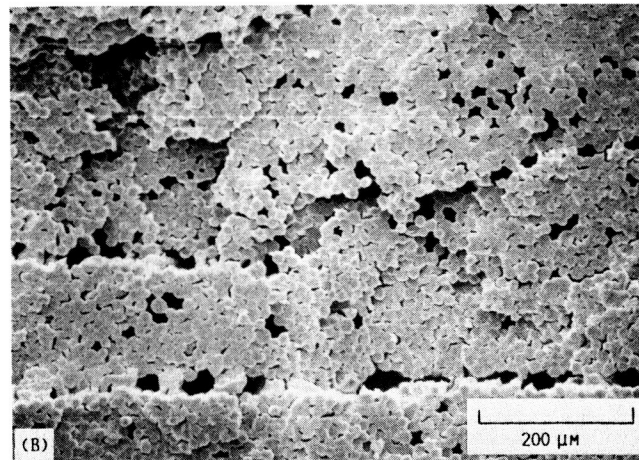
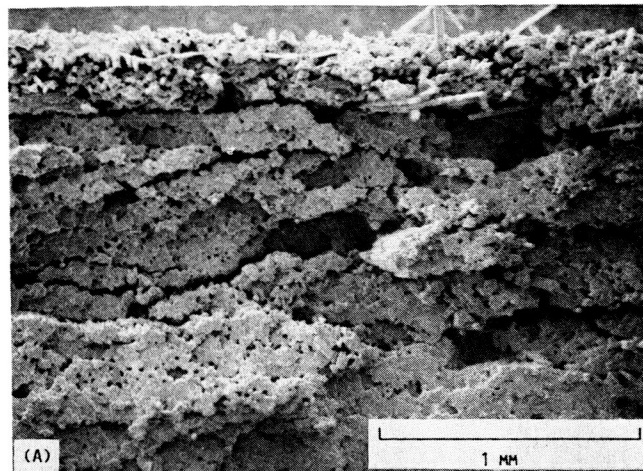


FIGURE 14. - FRACTURE SURFACES OF NICALON/SILSESQUIOXANE COMPOSITES HEATED TO (A) 1000, (B) 1200, AND (C) 1400 °C, THEN FRACTURED AT ROOM TEMPERATURE IN THREE-POINT BENDING.

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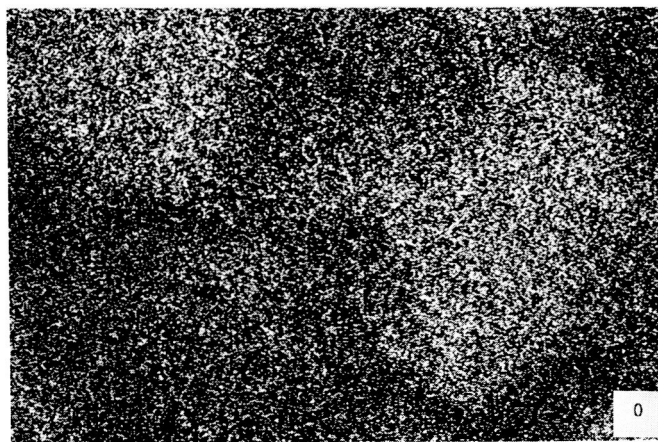
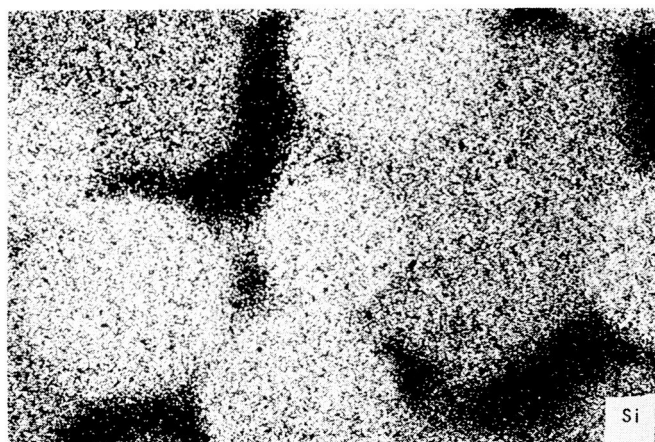
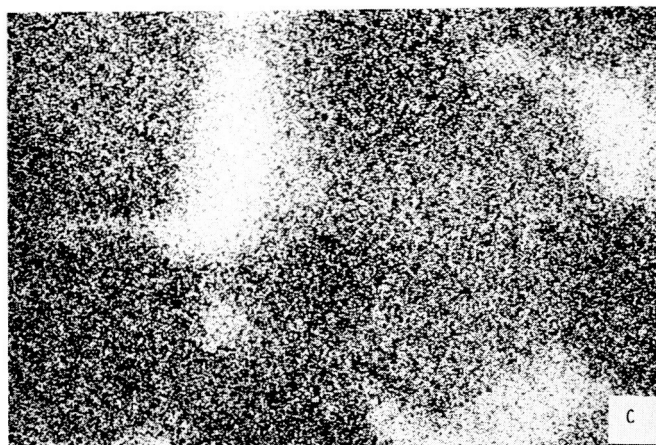
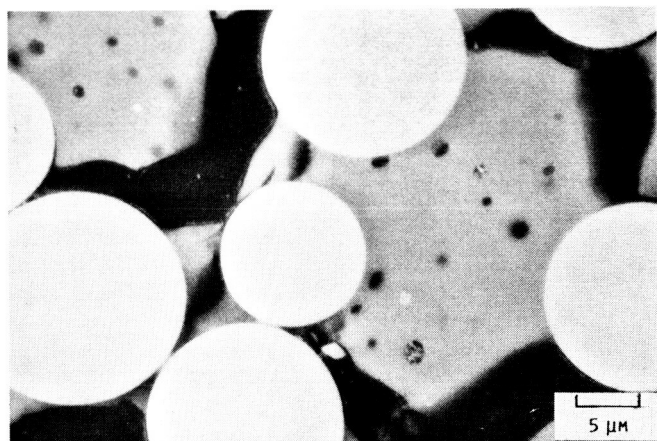


FIGURE 15. - ELEMENTAL COMPOSITION BASED ON EDS AND WDS OF NICALON/SILSESQUIOXANE COMPOSITE HEATED TO 1200 °C IN ARGON.

1. Report No. <b>NASA TM-89893</b>		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  <b>Silsesquioxanes as Precursors to Ceramic Composites</b>				5. Report Date	
				6. Performing Organization Code <b>506-43-11</b>	
7. Author(s)  <b>Frances I. Hurwitz, Lizabeth H. Hyatt, Joy Gorecki, and Lisa D'Amore</b>				8. Performing Organization Report No. <b>E-3581</b>	
				10. Work Unit No.	
9. Performing Organization Name and Address  <b>National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135</b>				11. Contract or Grant No.	
				13. Type of Report and Period Covered <b>Technical Memorandum</b>	
12. Sponsoring Agency Name and Address  <b>National Aeronautics and Space Administration Washington, D.C. 20546</b>				14. Sponsoring Agency Code	
15. Supplementary Notes <b>Prepared for the 11th Annual Conference on Composites, Advanced Ceramics, and Composite Materials cosponsored by the American Ceramic Society, DOD, and NASA, Cocoa Beach, Florida, January 18-23, 1987. Frances I. Hurwitz, NASA Lewis Research Center; Lizabeth H. Hyatt, Case Western Reserve University, Dept. of Chemical Engineering, Cleveland, Ohio 44106; Joy Gorecki, Case Western Reserve University, Dept. of Macromolecular Science and Summer Student Intern at NASA Lewis Research Center; Lisa D'Amore, Case Western Reserve University, Dept. of Chemical Engineering and Summer Student sponsored by the Society of Women Engineers.</b>					
16. Abstract  <b>Silsesquioxanes having the general structure <math>RSiO_{1.5}</math>, where R = methyl, propyl, or phenyl, melt flow at 70 to 100 °C. Above 100 °C, free -OH groups condense. At 225 °C further crosslinking occurs, and the materials form thermosets. Pyrolysis, with accompanying loss of volatiles, takes place at nominally 525 °C. At higher temperatures, the R group serves as an internal carbon source for carbo-thermal reduction to SiC accompanied by the evolution of CO. By blending silsesquioxanes with varying R groups, both the melt rheology and composition of the fired ceramic can be controlled. Fibers can be spun from the melt which are stable in argon to 1400 °C. The silsesquioxanes also have been used as matrix precursors for Nicalon and <math>\alpha</math>SiC platelet reinforced composites.</b>					
17. Key Words (Suggested by Author(s))  <b>Silsesquioxanes; Ceramic fibers, Ceramic matrix composites</b>				18. Distribution Statement  <b>Unclassified - unlimited STAR Category 24</b>	
19. Security Classif. (of this report) <b>Unclassified</b>		20. Security Classif. (of this page) <b>Unclassified</b>		22. Price* <b>A02</b>	
				21. No. of pages <b>15</b>	