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Stoichiometry control of SiOC ceramics by siloxane polymer functionality

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The guidelines, or empirical rules, previously described in the literature to estimate ceramic compositions from preceramic polymer compositions have been refined and quantified. Thermogravimetric and residual gas analyses of the pyrolysis of organosilsesquioxane polymers have identified the organic degradation products at various temperatures and indicated that essentially all of the silicon and oxygen atoms of these highly branched polymers are retained in the 1200 °C ceramic residue. Series of organosilsesquioxanes with systematically varied amounts of organosilsesquioxane and endcapping components were synthesized, cured, and pyrolyzed to 1200 °C under an inert atmosphere. Multiple linear regression analysis was used to quantify the relationships between the amount of carbon retained in the ceramic residues and the mole fractions of the various organic components of the preceramic polymer, allowing for retention of the silicon and oxygen of the silsesquioxane. Specifically, a phenylsilsesquioxane fragment contributes an average of 3.94 carbons to the resulting ceramic material, vinylsilsesquioxane, 1.52 carbons, methylsilsesquioxane, 0.59 carbons and a vinyldimethylsilyl endcapping group, 2.75 carbons. The utility of the model was shown by employing this information to predict a select set of candidate precursors to an SiOC with a carbon content near a desired 18 wt.% level. One of the candidate precursors $(MeSiO_{1.5})_{0.84}(Me_2ViSiO_{0.5})_{0.16}$ (predicted to afford an SiOC at 18.1 wt.% carbon) was then prepared, cured, pyrolyzed and analyzed to test the accuracy of the model. The 1200 °C ceramic was found to have 18.4 wt.% carbon, indicating good agreement between the actual and predicted values.

The composition of a ceramic material dictates many of its performance properties. For example in utilizing a polymer as a binder for ceramic powders in high density monoliths it is important to employ a siloxane-based polymer that provides a sufficient amount of excess, or free, carbon in its '$SiC+C_x$' pyrolysis products for effective sintering to occur.[1] A nearly linear dependence has been observed between the amount of free carbon in these ceramics and the amount of phenyl groups in the corresponding silsesquioxane precursors.[2] For SiOC materials the stoichiometry of the component elements has been shown to influence the stability of the ceramic towards oxidation.[3] Pyrolysis of specific silsesquioxane-based precursors has the potential to produce oxidatively resistant ceramic fiber-reinforced SiOC-matrix composites.[4] Recently we have explored the application of similar SiOC ceramic materials as anodes for rechargeable lithium ion batteries. Our initial results indicate that the elemental composition of these materials has great influence over the performance of a rechargeable battery by affecting the anode efficiency.[5]

In previous studies on SiOC precursors, a number of workers have examined the pyrolysis chemistry of precursors that give 'ultrahigh' ceramic yields,[6] or employed very elegant precursors such as block and graft copolymers,[7] or precursors that contained preformed polyhedral silsesquioxane cages.[8] In no case, however, is the initial chemical environment of silicon in siloxane polymers maintained beyond 500 °C. Scrambling, or redistribution, of the elements bound to silicon (carbon and oxygen) has been observed by ^{29}Si MAS NMR.[2,9] This pyrolysis chemistry, therefore, makes it difficult to quantitatively correlate the SiOC composition to that of the polymer. Others have attempted to influence the composition and the structure of SiOC glasses derived from polymeric silsesquioxane-based precursors. To minimize the amount of excess carbon present, ceramic glasses have been produced from precursors with high levels of Si—H functionality,[10] or from precursors designed to give glasses with low O/Si ratios.[11]

Several techniques have been employed to probe the local environment of silicon atoms and its impact on the broader nano- and micro-structure of such SiOC glasses. The pore structure has been characterized by BET analysis[12] and a number of authors have augmented ^{29}Si MAS NMR studies with X-ray diffraction and TEM analysis.[2,13] FTIR[14] and XPS spectroscopies[15] have also been used to provide information on the bonding arrangement about the silicon in these SiOC glasses. Perhaps the best description of the SiOC glass is that it is a random distribution of Si—O and Si—C bonds with no Si—Si or C—O bonds and the carbon not bonded to silicon participates in C—C bonds.[15,16] It has also been suggested that the local environment of the silicon in the SiOC glasses is predetermined by the silicon to oxygen ratio in the polymeric precursor.[15]

Determination of the distribution of local environments around silicon atoms, however, does not sufficiently explain the physical properties or performance characteristics of SiOC ceramics in key applications. Materials with similar silicon to oxygen ratios, but with differing amounts of carbon, have been shown to exhibit different X-ray diffraction patterns, oxidative stability, and electrochemical behavior.[3,5b] We believe that many, if not all, of these properties for specific applications are controlled by the overall stoichiometry and structure of the glasses and not strictly by the local environment about the silicon centers.

For this reason guidelines have been developed over the years to aid in the selection of appropriate preceramic polymers that will afford ceramics with defined compositions:[17]

(*i*) All aliphatic organic groups each contribute an amount of carbon equivalent to that contributed by a methyl group, presumably due to facile β-bond cleavage.[18b]

(*ii*) Unsaturated organic groups, such as aryl and alkylene groups, contribute substantial amounts of their carbon to a ceramic.[18]

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We believe these guidelines apply to silsesquioxane-type substituents broadly and consistently enough that they can be reduced to mathematical relationships that in turn can define a set of candidate preceramic polymers to afford a specified SiOC ceramic composition upon pyrolysis. The results reported here provide a basis set of empirical data from which such a model can be derived. The model is also validated by demonstrating the production of a ceramic with a predefined amount of carbon from a preceramic polymer candidate suggested by the model.

Results and Discussion

Range of silsesquioxane polymers

Silsesquioxane materials modified with endcapping moieties are useful ceramic precursors because both the backbone structure and the type and amount of organic functionality can be easily varied. The mole fraction of endcapping groups should be at least 0.10 to avoid extensive gelation in the synthesis, particularly of the polymers with high amounts of methylsilsesquioxane groups, but should remain below 0.40 to retain enough branching in the silsesquioxane backbone structure to provide sufficient ceramic conversion (char) yield. A variety of organic functionalities can also be included to provide for crosslinking, or cure, of the polymer. We prefer the inclusion of some vinyl groups to enable radical-initiated cure of the polymers for retention of shape and bulk integrity during pyrolysis.

Four series of preceramic silsesquioxane-based polymers were synthesized. Polymer composition was determined by ^{1}H and ^{29}Si NMR analysis (^{29}Si NMR spectra representative of series I–III are shown in Fig. 1) and is described by normalizing to one polymer equivalent which, by our convention, is defined as 1 mole of Si. Molecular weight distribution was determined by GPC and softening point by thermal mechanical analysis (TMA) (Table 1).

Series I: $(PhSiO_{1.5})_x(MeSiO_{1.5})_{0.75-x}(Me_2ViSiO_{0.5})_{0.25}$

($x = 0$–0.75 in 0.05 increments)

Series II: $(PhSiO_{1.5})_x(ViSiO_{1.5})_{0.75-x}(Me_2ViSiO_{0.5})_{0.25}$

($x = 0.05$–0.75 in 0.10 increments)

Series III: $(ViSiO_{1.5})_x(MeSiO_{1.5})_{0.75-x}(Me_2ViSiO_{0.5})_{0.25}$

($x = 0.05$–0.75 in 0.10 increments)

Series IV: $(ViSiO_{1.5})_{(1-x)/2}(MeSiO_{1.5})_{(1-x)/2}(Me_2ViSiO_{0.5})_x$

($x = 0.1$–0.35 in 0.05 increments)

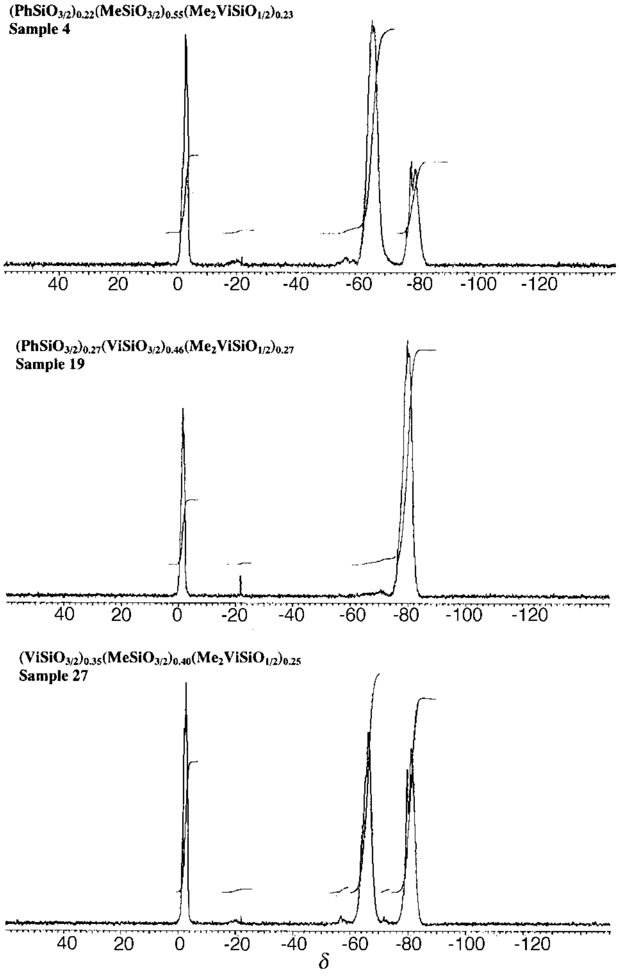

Fig. 1 ^{29}Si NMR of representative polymers of series I–III

Silicon and oxygen contents of ceramic

The silicon and oxygen contents of SiOC glasses derived from cured samples of these polymers can be anticipated based on conclusions arising from previously reported thermogravimetric and residual gas analyses (TGA/RGA) of these materials.[9a,19] The RGA of sample **4**, $(PhSiO_{1.5})_{0.22}$-$(MeSiO_{1.5})_{0.55}(Me_2ViSiO_{0.5})_{0.23}$, is considered typical of those observed for materials we have examined and is reproduced here (Fig. 2) to aid in the following discussion. The TGA weight loss curve and derivative curve shown in the bottom panel of Fig. 2 indicate that decomposition begins at approximately 400 °C and is essentially complete by 800 °C, affording a ceramic yield of greater than 80 wt.%. The profile of evolution of key volatile pyrolysis by-products shown in the top five panels indicate that the first volatiles evolved (at *ca.* 400 °C) are associated with vinyl groups, while those associated with phenyl groups and methyl groups are observed only at temperatures above 500 and 600 °C respectively. Hydrogen gas evolution begins near 500 °C and is evident throughout the remainder of the pyrolysis; negligible hydrogen is typically retained in SiOC ceramics derived from silsesquioxanes.[17]

TGA/RGA analyses of two other cured silsesquioxane samples from these series that afford nearly identical 1200 °C ceramic compositions yet have very different polymer composition (samples **16** and **30**) show nearly identical decomposition temperatures for the different organic groups and vary only in the amount of each type of volatile evolved in a manner that is proportional to the amount of associated organic group in the polymer.[17] In each case, all observed volatile materials were derived from the organic substituents of the polymers; no silicon- or oxygen-containing volatiles were observed. This contrasts with reports of RGA on other silsesquioxane gels;[9a] these differences may be due to higher amounts of crosslinking in the cured silsesquioxanes we have examined afforded by the highly branched structure, low silanol content and the vinyl functionality. This strongly suggests that all of the backbone elements of the silsesquioxanes reported here are retained in the resulting ceramic product.

The general conclusions that we have drawn from these TGA/RGA experiments are: (*a*) samples of these polymers cured by radical-initiated polymerization of their vinyl groups show thermal stability up to 400 °C; (*b*) the organic substituent with the lowest thermal stability is either the vinyl group or the silethylene group resulting from polymerization of the vinyl groups; (*c*) the only decomposition products observed are derived from the organic substituents, and (*d*) silsesquioxane structural elements (Si, O) are retained quantitatively in the 1200 °C ceramics. The assumption that all silicon and oxygen atoms remain in the material throughout the pyrolysis leads

Table 1 Preceramic polymer characterization

	composition by ^{29}Si NMR analysis[a] (mole fraction)						GPC	
sample	Ph-T	Vi-T	Me-T	Vi-M	polymer equiv. wt.[a]	T_g/°C	M_n	M_w
Ph/Me series								
1	0.06	—	0.70	0.24	77.1	26.3	2450	25300
2	0.12	—	0.70	0.18	79.3	34.6	2020	6830
3	0.17	—	0.62	0.21	83.1	24.0	1560	4690
4	0.22	—	0.55	0.23	86.8	31.8	1310	3860
5	0.29	—	0.51	0.20	90.3	52.3	7330	14500
6	0.34	—	0.44	0.22	94.0	63.0	5070	10800
7	0.38	—	0.39	0.23	96.7	56.9	3080	7120
8	0.43	—	0.34	0.23	99.8	47.1	2870	6300
9	0.50	—	0.31	0.19	103.1	63.1	2430	5350
10	0.50	—	0.23	0.27	105.2	22.2	1920	3400
11	0.53	—	0.21	0.26	106.8	32.2	2320	4680
12	0.62	—	0.12	0.26	112.4	29.4	2150	3820
13	0.66	—	0.08	0.26	114.9	32.3	1970	3250
14	0.70	—	0.06	0.24	116.8	30.1	1990	3200
15	0.74	—	0.00	0.26	119.8	21.3	1470	1880
Ph/Vi series								
16	0.00	0.77	—	0.23	82.4	−23.4	1860	5530
17	0.13	0.64	—	0.23	88.9	−7.1	1230	3440
18	0.22	0.55	—	0.23	93.4	−19.3	6490	13500
19	0.27	0.46	—	0.27	96.4	0.2	1770	5360
20	0.41	0.33	—	0.23	100.5	4.0	1860	4780
21	0.55	0.26	—	0.23	112.8	8.8	1500	3510
22	0.60	0.19	—	0.22	113.1	17.7	1280	2610
23	0.73	0.03	—	0.24	119.1	22.3	1230	2320
Vi/Me series								
24	—	0.06	0.71	0.23	73.8	−3.2	1920	5650
25	—	0.14	0.61	0.25	75.3	4.5	2580	27900
26	—	0.25	0.51	0.24	76.4	−12.0	2490	14000
27	—	0.35	0.40	0.25	77.8	−12.5	2110	7420
28	—	0.46	0.29	0.25	79.2	−3.3	2860	36400
29	—	0.56	0.19	0.25	80.4	−15.5	2060	6810
30	—	0.66	0.09	0.25	81.6	−28.2	1840	4560
31	—	0.77	0.00	0.23	82.4	−23.4	1860	5530
Me_2Vi series								
32	—	0.46	0.43	0.11	75.5	22.5	876	5650
33	—	0.39	0.39	0.22	77.5	5.3	1260	6880
34	—	0.36	0.37	0.27	78.5	−10.6	1520	9560
35	—	0.33	0.31	0.36	80.5	−33.5	863	2250

[a] Composition normalized to one polymer equivalent, defined by our convention as one mole of Si.

to a simplified estimate of the amount of these elements remaining in the ceramic.

Based on these observations, the prediction of the silicon and oxygen contents of SiOC ceramics becomes trivial; each mole of these elements present in the preceramic polymer can be assumed to be retained in the resulting ceramic. Employing the formula convention shown in Table 1, each equivalent of polymer contributes one mole of silicon. Each silsesquioxane unit contributes 1.5 moles of oxygen, and each endcapping unit contributes 0.5 moles of oxygen, to the SiOC ceramic.

The amount of carbon retained in these SiOC ceramics, however, is not obvious from the TGA/RGA experiments. Instead, empirical carbon analysis on ceramics resulting from 1200 °C pyrolysis of samples across the series of materials studied was employed, to form a basis set for a mathematical model describing the contributions of carbon to these ceramics from each type of polymer unit.

Generation of the basis set and mathematical model

Cured samples of each of the polymer precursors were pyrolyzed in bulk to 1200 °C under an inert atmosphere. The ceramic yield and elemental analysis of each of the resulting SiOC ceramics are summarized in Table 2. For most samples the material accounted for in the Si, C, and O analyses totals between 95 and 98%. It is our experience that the greatest error in the elemental analysis of these ceramics occurs in the silicon analysis; since this analysis depends on chemical digestion of the ceramic, incomplete digestion can lead to an artificially low values for silicon content in these materials.

A SAS statistical package was used to correlate the 35 empirical carbon elemental analyses for all of these ceramic materials to their polymer composition using multiple linear regression analysis (without intercept). Coefficients of carbon retention for each of the organic-containing moieties were calculated [eqn. (1)].

$$\begin{aligned}&\text{Moles of C in the SiOC per equivalent of polymer}\\&=3.94\times(\text{mole fraction Ph-T})\\&\quad+1.52\times(\text{mole fraction Vi-T})\\&\quad+0.59\times(\text{mole fraction Me-T})\\&\quad+2.75\times(\text{mole fraction Vi-M})\\&r^2=0.9976 \text{ for the 35 points examined}\end{aligned}\tag{1}$$

This can be interpreted as 76% of the carbon in a vinylsilsesquioxane group is retained in the SiOC (1.52 out of 2 C). 68.7% of the carbon in a vinyldimethylsiloxy group is retained in the SiOC (2.75 out of 4 C). 65.6% of the carbon in a phenylsilsesquioxane group is retained in the SiOC (3.94 out

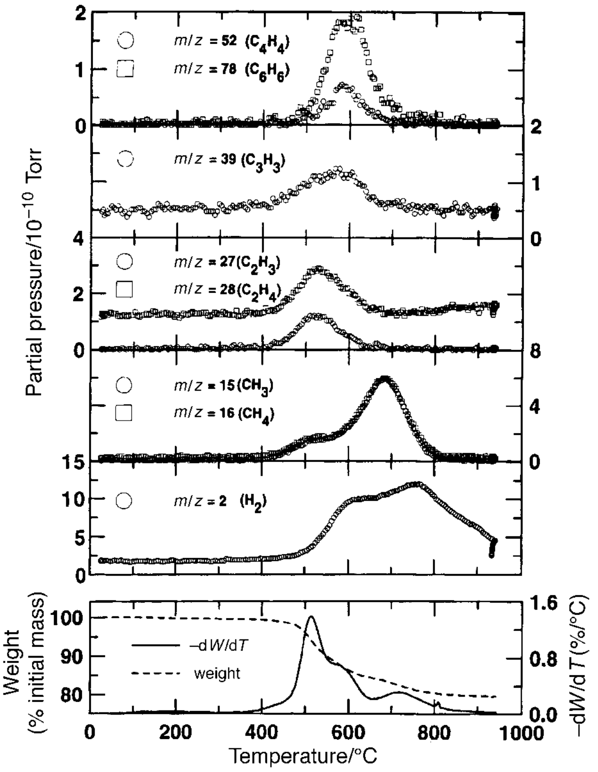

Fig. 2 TGA/RGA of sample **4**

of 6 C). 59% of the carbon in a methylsilsesquioxane group is retained in the SiOC (0.59 out of 1 C).

Although the TGA/RGA results show that the first organic decomposition products are associated with vinyl groups, these same groups contribute the highest percentage of carbon to the resulting ceramic, presumably due to their participation in crosslinking during polymer cure. Inversely, although methyl groups appear to be the most thermally stable of the groups studied here, they are more quantitatively lost during pyrolysis to 1200 °C.

The endcapping units in the polymer contains both vinyl and methyl groups. Whether the contribution of these groups to the carbon in the ultimate SiOC ceramic is identical to the contribution of the same groups on silsesquioxane units is not known, but the observed coefficients are consistent with this possibility [eqn. (2)].

$$\begin{aligned}1\ \text{mol Me}_2\text{ViSi} &= 2\ \text{mol Me} + 1\ \text{mol Vi}\\ &= 0.59 \times 2\ \text{mol Me} + 1.52 \times 1\ \text{mol Vi}\\ &= 2.70\ \text{mol C} \qquad (2)\end{aligned}$$

This can be compared with an observed value of 2.75 mol C/equiv. Me_2ViSi.

The degree of fit of the model to all the experimental data was determined by comparing the elemental analysis observed for the SiOC ceramics derived from the cured polymers in these series to that predicted by the model (Table 2, Fig. 3–5). The correlation between the observed wt.% of the components in the SiOC and that predicted by the model shows that the fit is excellent. This is especially true with the wt.% C content, where the correlation gives an overall r^2 value of 0.9976. Although the calculated and measured values for silicon and oxygen are generally within the experimental error associated with this analytical method (2.5 wt.%), the model consistently predicts a value higher than that actually measured, particularly for silicon. This does not necessarily indicate a violation of the assumption that no silicon and oxygen atoms are lost during pyrolysis; rather we believe it can be attributed to incomplete digestion in the method used to analyze silicon.

Table 2 Ceramic elemental analysis, actual and predicted values

		elemental analysis (wt.%)			predicted by model (wt.%)		
sample	ceramic yield (wt.%)	Si	O	C	Si	O	C
Ph/Me series							
1	81.2	42.4	30.2	24.6	43.9	31.5	24.6
2	83.9	39.8	29.5	26.8	42.7	32.1	25.2
3	81.8	39.4	28.9	30.0	41.2	30.3	28.4
4	82.3	37.9	26.9	32.5	40.0	28.9	31.1
5	80.8	36.6	26.1	33.5	38.6	28.6	32.9
6	81.6	35.4	25.4	36.2	37.4	27.3	35.3
7	80.6	34.1	24.9	38.0	36.6	26.5	36.9
8	80.5	33.7	23.5	39.7	35.7	25.8	38.5
9	80.7	31.9	23.6	40.9	34.6	25.8	39.6
10	80.2	31.6	22.2	41.1	34.3	24.0	41.7
11	80.3	30.5	21.7	43.9	33.8	23.9	42.3
12	77.8	31.1	21.3	44.4	32.4	22.9	44.7
13	78.4	29.3	20.8	46.0	31.8	22.5	45.7
14	76.0	29.8	21.9	47.0	31.3	22.5	46.2
15	72.7	30.2	20.0	49.3	30.7	21.7	47.6
Ph/Vi series							
16	86.1	38.1	26.8	31.1	40.1	29.0	30.9
17	85.2	36.2	26.1	34.8	38.0	27.5	34.4
18	84.1	33.8	24.8	37.4	36.7	26.6	36.7
19	83.0	33.3	22.8	40.5	36.1	25.3	38.6
20	81.7	32.8	23.1	41.2	34.8	24.3	40.9
21	80.0	29.0	22.0	44.0	32.0	24.3	43.7
22	75.9	28.9	22.5	45.7	31.9	23.6	44.5
23	73.2	29.2	21.9	46.5	30.8	22.1	47.1
Vi/Me series							
24	79.9	46.8	31.0	21.7	45.2	32.7	22.1
25	81.1	44.6	29.7	23.1	44.4	31.6	23.9
26	83.3	42.0	29.5	24.6	43.7	31.3	25.0
27	84.2	41.5	29.6	25.2	42.8	30.5	26.6
28	84.4	40.7	28.1	27.1	42.1	29.9	28.0
29	85.0	39.5	27.7	28.7	41.4	29.5	29.2
30	85.8	38.3	27.7	30.2	40.7	29.0	30.3
31	86.1	38.1	26.8	31.1	40.1	29.0	30.9
Me_2Vi series							
32	82.2	38.2	32.6	26.1	42.9	34.0	23.0
33	80.4	39.3	28.8	27.4	42.7	31.2	26.1
34	75.1	40.4	28.0	29.2	42.6	29.9	27.5
35	68.4	42.5	27.6	29.6	42.3	27.5	30.3

Validation of the model

In an effort to validate the model, an experiment was designed in which the model was used to provide a series of suggested polymer compositions predicted to afford, upon pyrolysis to 1200 °C, SiOC ceramics with a carbon content near 18 wt.%. The value of 18 wt.% was chosen since this was a carbon level that was outside the range of composition employed to generate the model, thus demonstrating the credibility of the model for compositions outside this range. The lowest wt.% carbon used in generating the model was 22 wt.% (from sample **24**). The results of this experiment are given here and the details of the polymer and its pyrolysis are provided in the experimental section.

Validation of this model was provided by demonstrating that one of the candidate polymer compositions predicted to produce a 1200 °C ceramic with a desired carbon content actually does so. A list of candidate preceramic polymers was created by the model (in mole fraction increments of 0.05) that were predicted to produce a ceramic containing approximately 18 wt.% carbon in an SiOC after 1200 °C pyrolysis under an inert atmosphere (Table 3). Selecting from this set of candidates we prepared $(MeSiO_{1.5})_{0.84}(Me_2ViSiO_{0.5})_{0.16}$ (example **d**), cured a sample with peroxide and pyrolyzed it to 1200 °C under an inert atmosphere. The resulting ceramic was found to have a carbon content of 18.4 wt.%, very close to the 18.1 wt.% predicted by the model. This example serves to validate the approach of using such a model to identify

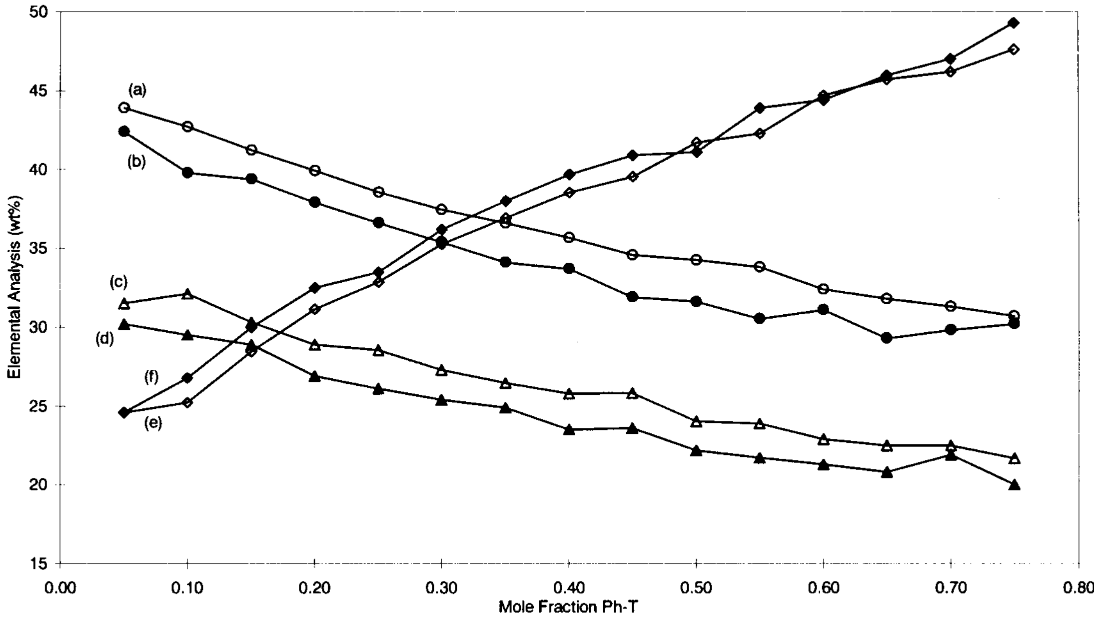

Fig. 3 Comparison of predicted and actual elemental analyses for Ph/Me series. (a) predicted Si, (b) actual Si, (c) predicted O, (d) actual O, (e) predicted C, (f) actual C.

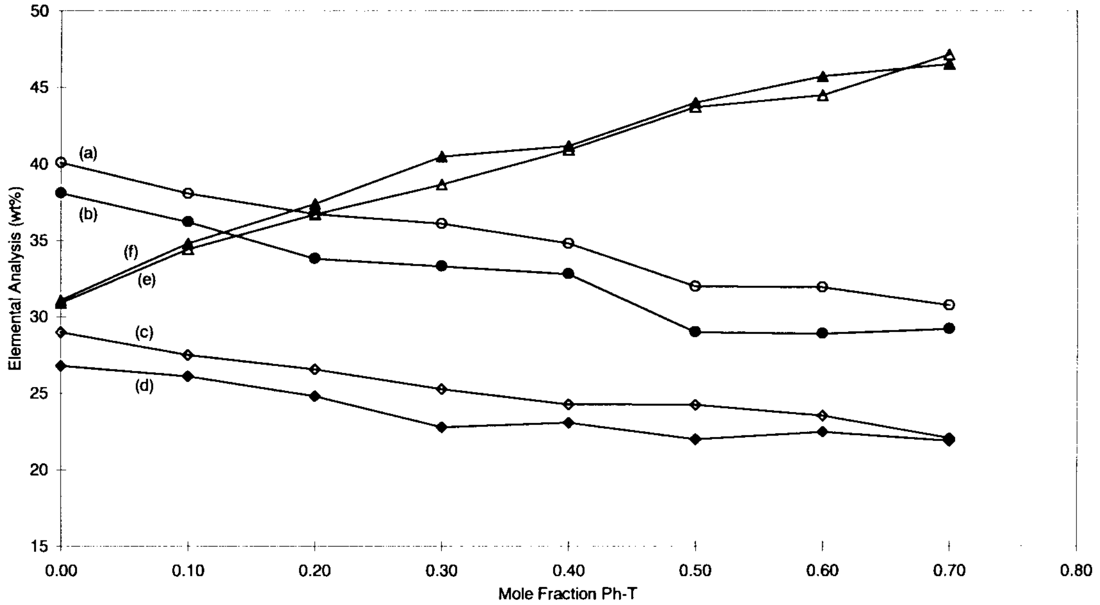

Fig. 4 Comparison of predicted and actual elemental analyses for Ph/Vi series. (a) Predicted Si, (b) actual Si, (c) predicted O, (d) actual O, (e) predicted C, (f) actual C.

potential preceramic polymers for desired ceramic compositions with minimal synthetic effort.

Summary

The guidelines previously reported in the literature for estimating ceramic composition from preceramic polymer composition have been refined and quantified. Thermogravimetric and residual gas analyses of the pyrolysis of organosilsesquioxane polymers have identified the organic degradation products at various temperatures and indicated that essentially all of the silicon and oxygen atoms of the polymer framework are retained in the 1200 °C ceramic residue.

A series of silsesquioxanes with systematically varying amounts of organosilsesquioxane and endcapping components were synthesized, cured and pyrolyzed to 1200 °C under an inert atmosphere. Multiple linear regression was used to quantify the relationship between the amount of carbon retained in the ceramic residues and the mole fractions of the various components of the preceramic polymer, allowing for retention of the framework silicon and oxygen. Specifically, phenylsilsesquioxane fragments contribute an average of 3.94 carbons to the resulting ceramic material, vinylsilsesquioxane 1.52 carbons, methylsilsesquioxane, 0.59 carbons and a vinyldimethylsilyl endcapping group, 2.75 carbons.

The utility of the model was shown by employing this information to arrive at a selected number of candidate precursors to an SiOC of a desired (18 wt.% carbon) composition. One of the candidate precursors $(MeSiO_{1.5})_{0.84}$-$(Me_2ViSiO_{0.5})_{0.16}$ (predicted to have 18.1 wt.% carbon) was then prepared, cured, pyrolyzed and analyzed to test the accuracy of the model. The 1200 °C ceramic was found to have 18.4 wt.% carbon, indicating good agreement between the actual and predicted values.

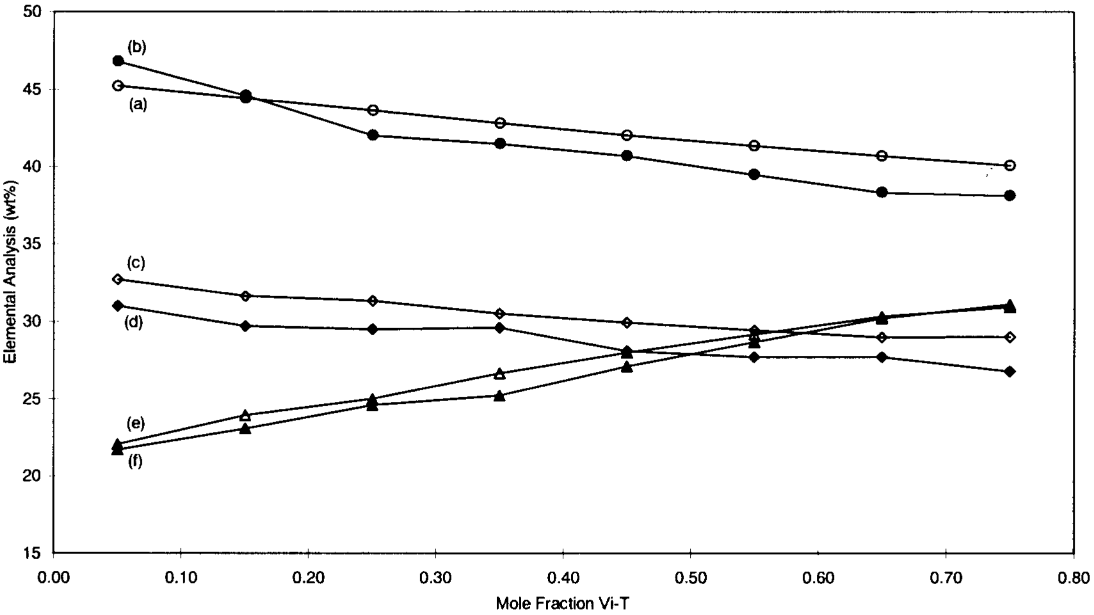

Fig. 5 Comparison of predicted and actual elemental analyses for Vi/Me series. (a) Predicted Si, (b) actual Si, (c) predicted O, (d) actual O, (e) predicted C, (f) actual C.

Table 3 Candidate preceramic polymers for a *ca.* 18 wt.% carbon ceramic

	candidate polymer composition (mole fraction)				estimated ceramic elemental composition (mol%)			actual (mol%)
sample	Ph-T	Vi-T	Me-T	Vi-M	Si	O	C	C
a	0.00	0.00	0.90	0.10	46.7	37.2	16.1	
b	0.00	0.05	0.85	0.10	46.3	36.9	16.9	
c	0.00	0.10	0.80	0.10	45.8	36.6	17.6	
d	0.00	0.00	0.85	0.15	46.3	35.6	18.1	18.4
e	0.00	0.15	0.75	0.10	45.4	36.2	18.4	
f	0.05	0.00	0.85	0.10	45.2	36.0	18.8	
g	0.00	0.05	0.80	0.15	45.9	35.3	18.8	
h	0.00	0.20	0.70	0.10	45.0	35.9	19.1	
i	0.05	0.05	0.80	0.10	44.8	35.7	19.5	
j	0.00	0.10	0.75	0.15	45.5	35.0	19.6	
k	0.00	0.25	0.65	0.10	44.6	35.6	19.8	

Experimental

Materials and methods

All of the methoxysilane, disiloxane and chlorosilane starting materials were obtained as high purity intermediates from Dow Corning Corporation. Trifluoromethanesulfonic acid and trifluoroacetic acid were purchased from Aldrich Chemical and used without further purification. Toluene, calcium carbonate, sodium hydrogencarbonate, potassium hydroxide and Celatom filter aid were purchased from Fischer Scientific and used as provided. Lupersol 101® was purchased from Lucidol Chemical Company.

The polymers were characterized by softening point, as measured with an Omnitherm TMA, molecular weight and molecular weight distribution employing a Waters GPC with polystyrene standards and refractive index detection, and ^{1}H and ^{29}Si NMR spectroscopy, employing a Varian 200 and 400 MHz NMR spectrometer. The characterization for all of the polymers studied is given in Table 1.

Aliquots of all of the polymers studied were cured by mixing the polymer with 1 wt.% Lupersol 101 peroxide and heating the resulting mixture to 175 °C under argon. Aliquots of the cured polymers were then converted into SiOC ceramics by pyrolysis in a Lindberg Model 54434 or similar tube furnace fitted with Eurotherm or similar temperature controllers. The pyrolysis was conducted under high purity argon gas at a purge rate sufficient to prevent decomposition and redeposition of the vapors that were evolved during the pyrolysis (*ca.* 30 turnovers h^{-1}). The samples were placed in alumina boats, and transferred to the pyrolysis tube which was then sealed from the atmosphere and flushed with argon for 30 min prior to beginning the pyrolysis. The temperature was raised at 5 °C min^{-1} to the hold temperature of 1200 °C and held there for 1 h. The samples were then cooled to ambient temperature at a rate of *ca.* 10 °C min^{-1}. Samples were weighed before and after the pyrolysis to calculate the ceramic conversion (char) yield (Table 2).

The SiOC ceramic was ground into a fine powder with a synthetic sapphire mortar and pestle prior to elemental analysis. The CHN analyses were carried out on a Perkin Elmer 2400 analyzer. Oxygen analyses were done on a Leco oxygen analyzer (model R0–316) equipped with an oxygen determinator 316 (model 783700) and an electrode furnace EF100. Silicon analyses were determined by a fusion technique which consisted of converting the solid to a soluble form and analyzing the solute for total silicon by Analytical Research Laboratories 3580 ICP-AES analysis.

The decomposition process of the polysiloxane was studied using a TA Instruments model 51 thermal gravimetric analyzer (TGA) connected to a Leybold Quadrex 200 residual gas analyzer (RGA, mass spectrometer). Ultra-high purity argon was flowed at 25 cm^{3} min^{-1} over the polymer samples (between

50 and 70 mg) as they were heated. The argon stream exited the TGA and passed to the atmospheric pressure inlet of the RGA. A Vacoa (Vacuum Corporation of America Bohemia, New York, USA) leak valve was used to sample a small amount of the TGA exhaust and pass it to the mass spectrometer chamber. The base pressure of the RGA chamber is near 5×10^{-8} Torr and it was operated near 3×10^{-8} Torr with the leak valve open. Thus, the signal from the gases evolved during the polymer pyrolysis overwhelms those from the chamber alone. All gas flow lines were heated above 100 °C, to facilitate the transport of evolved vapors and minimize condensation. After loading the samples in the TGA, argon was flushed through the system until the base pressure in the RGA stabilized. The samples were then heated at a rate of 10 °C min^{-1} to 1000 °C while the sample weight and the evolved gases were monitored.

The modeling was performed by multiple linear regression analysis without intercept for 35 data points employing the SAS/STAT statistical package, version 6, Silicon SAS Institute, Cary, NC, USA.

Polymer synthesis: model generation

The following is a detailed description of the preparation of sample **1** but is also representative of the procedures followed for all of the polymers studied. In a 5 l three-necked round-bottomed flask fitted with an internal thermometer, a reflux condenser and an overhead stirrer were placed phenyltrimethoxysilane (77.0 g, 0.388 mol), methyltrimethoxysilane (742 g, 5.45 mol), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (192 g, 1.03 mol), trifluoromethanesulfonic acid (5.0 ml) and deionized water (50 g, 2.8 mol). This mixture was then heated to reflux with stirring for 2 h. Toluene (1.5 l) and deionized water (410 ml) were added to the mixture and the reaction mixture heated to reflux for an additional 2 h. Calcium carbonate (10 g) was added, the reflux condenser replaced with a distillation head and the distillate removed until the vapor head temperature reached 85 °C. Aqueous 3 wt.% potassium hydroxide (50 ml) was added, the distillation head replaced with a Dean-Stark trap and reflux condenser and the water azeotropically removed. After the reaction mixture was free of water (internal temperature above 105 °C), the reflux was continued for 8 h. The mixture was cooled to *ca.* 50 °C, and chlorodimethylvinylsilane (50 ml) was added. After stirring for approximately 16 h at ambient temperatures, the mixture was filtered through a sintered glass frit containing Celatom filter-aid. The solvent was removed from the filtrate by means of a rotary evaporator under reduced pressure affording >95% isolated yield of colorless polymer.

Polymer synthesis: model validation

In a 1 l three-necked round-bottomed flask fitted with an internal thermometer, a reflux condenser and an overhead stirrer were placed methyltrimethoxysilane (124 g, 0.912 mol), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (15 g, 0.080 mol), trifluoroacetic acid (0.5 g) and deionized water (0.25 g). This mixture was then heated to reflux with stirring for 2 h. After cooling, deionized water (80 g) was added to the mixture and the reaction mixture heated to reflux for an additional 2 h. Again after cooling, calcium carbonate (0.5 g) was added, the reflux condenser replaced with a distillation head and the distillate removed until the vapor head temperature reached 95 °C. Toluene (660 g) and aqueous 3 wt.% potassium hydroxide (12.5 g) was added, the distillation head replaced with a Dean–Stark trap and reflux condenser and the water azeotropically removed. After the reaction mixture was free of water (internal temperature above 105 °C), the mixture was cooled to 50 °C, and chlorodimethylvinylsilane (25 ml) was added. After stirring for approximately 16 h at ambient temperatures, the mixture was filtered through a sintered glass frit containing Celatom filter-aid. The solvent was removed from the filtrate by means of a rotary evaporator under reduced pressure affording an isolated yield of 57 g of a colorless polymer. Yield: 75% of theoretical. The exact molar composition of the polymer was determined to be $(CH_3SiO_{1.5})_{0.84}((CH_3)_2ViSiO_{0.5})_{0.16}$ by ^{29}Si and ^{1}H solution NMR spectroscopy in $CDCl_3$. The polymer had a softening point of 69.3 °C. The polymer (4.63 g) was dissolved in toluene (4.60 g), and an organic peroxide (Lupersol 101®, 0.10 g) was added. The solvent was removed by heating in an oven at 120 °C for 80 min under nitrogen, then free radical polymerization initiated by heating to 175 °C for 10 min under nitrogen to crosslink the polymer. The brittle crosslinked polymer was then crushed and placed in a large alumina boat and pyrolyzed to 1200 °C under argon to convert it into an SiOC ceramic. Yield: 82.1 wt.%. Elemental analysis Si, 39.7; O, 32.5; C, 18.4%.

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