

# On the phase composition of polymethylsiloxane derived ceramics

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The pyrolysis products of polymethylsiloxanes (PMS) have been studied in order to characterize their phase composition from the viewpoint of equilibrium thermodynamics. Dilatometry measurements and redox analyses with PbO have been conducted and the results analysed and compared with respect to the second law of thermodynamics. In agreement with equilibrium thermodynamics, which shows that there is no ternary compound in the Si–O–C system, the experimental results imply that the pyrolysis residue is an amorphous or nanocrystalline composite consisting of a SiO<sub>2</sub>-phase matrix with embedded SiC and C particles. These findings seem to contradict the accepted scientific opinion of ternary silicon-oxycarbide phases. © 1998 Kluwer Academic Publishers

## 1. Introduction

Polymers in which the silicon–oxygen bond represents the repeating unit in the backbone structure and characterized by the general formula  $[R_nSiO_{(2-0.5n)}]_m$  are referred to as siloxanes. Here R are groups such as hydrogen, methyl, vinyl and phenyl groups. The index  $n$  can take any value in the range  $1 \leq n < 3$  and describes the network structure of the polymer where the boundary structures are:  $n = 3$ , the dimer;  $n = 2$ , an unbranched chain; and  $n = 1$ , the three-dimensional network of a silicon resin. The index  $m$  denotes the number of repeating units connected together in one macromolecule and  $m$  ranges from several hundreds to several thousands. These compounds have been intensely examined [1–5] as precursors for polymer derived ceramics. The thermal degradation of polysiloxanes starts below 500 °C with the volatilization of gaseous species of low molecular weight. The highly crosslinked residue decomposes with increasing temperature, but the very stable Si–O bonds with a binding energy (BE) of 423 kJ per bond [6] remain intact. The weaker Si–R bonds are split and replaced by stable Si–C bonds with a BE = 439 kJ per bond [6]. As a result, hydrogen, gaseous hydrocarbons and a solid ceramic residue, named silicon oxycarbide glasses, containing the elements Si, O and C are formed [7–9]. Another way to produce these materials is the sol-gel route, as shown and examined by Hammond et al. [10] and Soraru and coworkers [11, 12].

The ceramic (composite) has shown interesting engineering properties, such as a low thermal expansion coefficient, refractoriness, high thermal and electrical conductivity, and nominal chemical homogeneity and purity. In order to understand and modify these properties it is necessary to describe the structure and phase composition of these ceramics.

The questions raised in this investigation are: How can this material be understood in terms of thermodynamics and phase distribution? Do Si–C and Si–O have true Si–O–C bonds or do they arrange into stable thermodynamic phases, i.e. SiO<sub>2</sub>, SiC and C, which are mixed homogeneously in the pyrolytic residue?

The use of conventional X-ray phase analysis is hindered by two factors. Firstly, up to temperatures of about 1200 °C, the pyrolysis products remain amorphous to X-ray phase analysis. Thus, there are no clear signals that can be compared to known substances (SiO<sub>2</sub> or SiC). Secondly, to date there are no X-ray data about ternary Si–O–C compounds available, which could serve as references.

Other methods such as <sup>29</sup>Si magic angle spinning–nuclear magnetic resonance (<sup>29</sup>Si-MAS-NMR) and X-ray photoelectron spectroscopy (XPS) show that silicon exists in various binding states, especially SiO<sub>4/2</sub>, SiCO<sub>3/2</sub>, SiC<sub>2</sub>O<sub>2/2</sub> and SiC<sub>4</sub> [13–15]. However, a severe drawback of these methods of analysis is that they do not allow the distinction between bulk and transition states, e.g. boundary layers, of the atoms examined, which is essential in the case of polysiloxanes.

<sup>13</sup>C- and <sup>1</sup>H-MAS-NMR and Raman spectroscopy indicate the presence of carbide-like and graphitic-like carbon [15]. The latter is similar to pyrolytic carbon with a turbostratic structure.

## 2. Experimental procedure

### 2.1. Sample preparation

(Poly-methyl-siloxane PMS, NH 2100, Hüls Silicone, Nuenchritz, Germany) forms a crosslinked structure through polycondensation of its hydroxy-functional groups. The repeating unit has the composition

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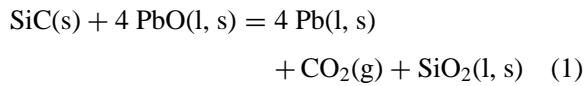
[CH<sub>3</sub>SiO<sub>1.5</sub>]. The polymer powder was pressed into discs 25 mm in diameter with a thickness of 5 mm in an uniaxial thermopress where it was simultaneously cured for 90 min at 250 °C and 20 MPa. The discs were then cut and were heated at 1 °C min<sup>-1</sup> to 1000 °C, held for 12 h and cooled back to room temperature at 10 °C min<sup>-1</sup>.

## 2.2. Dilatometer measurements

The linear thermal expansion of the bars received from pyrolysis was measured in a dilatometer (Netsch, Selb, Germany), which allowed for measurements in vacuum up to temperatures of 1800 °C. The results have been used to calculate the linear thermal expansion coefficient in the temperature range 20–400 °C.

## 2.3. Quantitative analysis of the SiC and C content of the pyrolysed PMS

In order to determine the content of SiC and C in the samples quantitatively, they were oxidized using lead oxide (PbO) following the reaction schemes



The reactions may be followed by measuring the parameters carbon dioxide pressure,  $P_{\text{CO}_2}$ , and the weight of the lead,  $m_{\text{Pb}}$ , developed.

Prior to analysis the samples were ground to powder and mixed with PbO in a weight ratio 1 : 100 (pyrolytic residue : PbO). The mixture was pressed into pellets and put into a vitreous silica crucible. This was then placed into a vitreous silica tube with known volume  $V_{\text{R}}$ , and evacuated to pressures below 0.1 MPa.

During heating in a closed system at a rate of 8 °C min<sup>-1</sup> from 400 to 880 °C, the development of CO<sub>2</sub>-gas is indicated by a pressure increase in the tube. Excess PbO combines with silica to form a glassy phase, which encapsulates any metallic lead formed by the redox reactions given in Equations 1 and 2. Cooling the melts rapidly to room temperature preserves the sharp boundary between glass and metal. The CO<sub>2</sub> pressure measured at room temperature,  $P_{\text{CO}_2}$ , allows calculation of the molar amount of gas produced,  $n_{\text{CO}_2}$ , by application of the ideal gas law

$$n_{\text{CO}_2} = \frac{P_{\text{CO}_2} \times V_{\text{R}}}{R \times T} \quad (3)$$

where  $R$  is the ideal gas constant ( $R = 8.313 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the measurement temperature (in this case, room temperature).

The amount of lead,  $n_{\text{Pb}}$ , has been determined by separating the metal from the glassy SiO<sub>2</sub>–PbO phase and weighing. The measured mass,  $m_{\text{Pb}}$ , and the molar

weight of lead,  $M_{\text{Pb}} = 207.2 \text{ g mol}^{-1}$ , allow the calculation of  $n_{\text{Pb}}$

$$n_{\text{Pb}} = \frac{m_{\text{Pb}}}{M_{\text{Pb}}} \quad (4)$$

The stoichiometry of Equations 1 and 2 leads to determining equations for  $n_{\text{C}}$ , Equation 5, and  $n_{\text{SiC}}$ , Equation 6

$$n_{\text{C}} = \frac{4n_{\text{CO}_2} - n_{\text{Pb}}}{2} \quad (5)$$

$$n_{\text{SiC}} = \frac{n_{\text{Pb}} - 2n_{\text{CO}_2}}{2} \quad (6)$$

where  $n_{\text{C}}$  and  $n_{\text{SiC}}$  are the amounts of carbon and silicon carbide contained in the sample, respectively. Assuming the balance of the pyrolysed PMS to be SiO<sub>2</sub>, one can calculate the weights of SiO<sub>2</sub>, SiC and C ( $M_{\text{SiO}_2} = 60 \text{ g mol}^{-1}$ ,  $M_{\text{SiC}} = 40 \text{ g mol}^{-1}$ ,  $M_{\text{C}} = 12 \text{ g mol}^{-1}$ ) as follows

$$n_{\text{SiO}_2} = \frac{m_{\text{S}} - n_{\text{SiC}} \times M_{\text{SiC}} - n_{\text{C}} \times M_{\text{C}}}{M_{\text{SiO}_2}} \quad (7)$$

## 3. Results and discussion

The linear thermal expansion coefficient in the temperature range 20–400 °C was found to be  $\alpha_{20-400\text{ °C}} = (4.5 \pm 0.3) \times 10^{-7} \text{ °C}^{-1}$ . This value is quite small compared with other ceramics or glasses. However, Brückner [16] measured a linear thermal expansion coefficient,  $\alpha$ , of vitreous silica annealed at 1000 °C of  $4.6 \times 10^{-7} \text{ °C}^{-1}$  in the range 20–200 °C.

Based on the method developed above, quantitative phase analysis with Equations 3–7 delivered the results given in Table I.

The calculations of the volume ratios do not take into account the overall porosity of the material, which is about 13 vol % measured with He-pycnometry (AccuPyc 1330, Micromeritics GmbH, Moenchengladbach, Germany). Considering these measured data and literature data [17, 18] one can calculate the linear thermal expansion coefficient of a composite material that is characterized by the data given in Table II. A value of  $4.9 \times 10^{-7} \text{ °C}^{-1}$  is obtained assuming a volumetric dependency.

Assuming that during pyrolysis neither silicon nor oxygen leaves the material as a gaseous species, the results of Table I can be compared with those predicted by idealized pyrolysis equations. In general, this is

$$\text{R}_n\text{SiO}_{(2-0.5n)} = (1 - 0.25n) \text{SiO}_2 + 0.25n \text{SiC} + x \text{C} + y \text{(hydrocarbon gases)} \quad (8)$$

TABLE I Quantitative phase analysis with PbO of PMS which was pyrolysed at 1000 °C in vacuum for 12 h

	SiO <sub>2</sub>	SiC	C
Weight %	73	17	10
Mol %	49	17	34
Volume ratio	1	0.15	0.13

TABLE II Measured values and literature data for the calculation of linear thermal expansion coefficient of the composite material

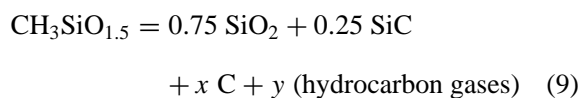
	Vitreous silica	Silicon carbide	Vitreous carbon	Porosity
Volume fraction	68	10.2	8.8	13
Linear thermal expansion coefficient [ $10^{-6} \text{ K}^{-1}$ ]	0.46	4.0	2.0–5.8	0
Source	[16]	[18]	[17]	

TABLE III Results of phase analysis with lead oxide compared with elemental analysis

	Quantitative analysis with PbO	elemental analysis <sup>a</sup>
PMS	$\text{R}_{1.01}\text{SiO}_{1.49}$	$\text{R}_{0.94}\text{SiO}_{1.53}$

<sup>a</sup>Datum courtesy of Fraunhofer Institut für Silcatforschung, Würzburg, Germany.

and for the special case of PMS



where  $x$  and  $y$  are coefficients dependent on the pyrolysis conditions and the siloxane resin used. Equation 9 yields a fixed ratio of  $n_{\text{SiO}_2}/n_{\text{SiC}} = 3$  for PMS. Using the data of Table I, we find  $n_{\text{SiO}_2}/n_{\text{SiC}} = 2.9$ , which is close to the theoretical value. As can be seen from Equation 8, we can find the index,  $n$ , of the raw material by solving

$$\frac{n_{\text{SiO}_2}}{n_{\text{SiC}}} = \frac{1 - 0.25n}{0.25n} \quad (10)$$

The results of this calculation have been compared with those received from elemental analysis of as-supplied polymeric PMS (Table III).

The correlation between the results is a strong indication for the validity of the values found by lead-oxide-based phase analysis. One reason for deviations that has to be taken into consideration is the fact that low molecular-weight fragments of the siloxane resin evaporate during pyrolysis and therefore change the effective composition of the raw material.

The second law of thermodynamics [19] states that the change in inner energy of any reaction is independent of the reaction route chosen. In this case this means that for the Si–O–C–(H) system of the siloxane resin, after complete removal of hydrogen above  $1000^\circ\text{C}$  one has to investigate either the ternary Si–O–C system or any of the binary systems for stable condensed phases, regardless of both the initial composition and the synthesis route.

The phase equilibria and chemical reaction in this system have been intensely studied for a long time [20–23]. The results of these works show that the only stable condensed compounds are SiC and  $\text{SiO}_2$ . Moreover Nickel [23] proposed the presence of liquid SiO at high temperatures and low oxygen partial pressure. The

existence of stable or metastable ternary compounds could not be proven.

The pyrolysis of siloxanes in vacuum after complete removal of hydrogen results in a material situated in the Si–O–C ternary system. Based on NMR measurements, these amorphous substances have been termed silicon-oxycarbide-glasses [15, 24–28] associated with a postulated metastable ternary Si–O–C phase.

However, coming from the quaternary Si–O–C–H system to the Si–O–C ternary system, on thermodynamic grounds the only stable condensed phases are those mentioned above. The quantitative phase analysis with PbO reveals that  $\text{SiO}_2$  is the major phase after pyrolysis, outweighing all other phases. Additionally, the dilatometer measurements show a linear thermal expansion coefficient of the pyrolysed material close to that of vitreous silica, which is about one order of magnitude smaller than that of SiC and C. Usually in any composite the matrix phase dominates the expansion behaviour, which is true for microparticulate composites as well as those on an atomic scale.

Taking into account these results, which support the thermodynamic viewpoint, we conclude that the real structure of pyrolysed PMS is an amorphous or nanocrystalline composite, with  $\text{SiO}_2$  as the matrix phase embedding SiC and C particles. The mixed coordination states found by  $^{29}\text{Si}$ -MAS-NMR and XPS can be attributed to boundary states between the very finely dispersed phases SiC, C and  $\text{SiO}_2$ . The material can be compared to other structures such as diamond, which are not stable but metastable in thermodynamic terms.

Based on knowledge of the phase content it is possible to analyse reactions of the polysiloxane derived ceramics such as the carbothermal reduction at temperatures above  $1400^\circ\text{C}$  or fibre matrix reactions as described by Gang Qi and Pantano [29]. Another example is the analysis of the decomposition reaction of PMS derived ceramics in alkaline aqueous solutions at elevated temperatures and high pressures, which result from the dissolution of the major phase,  $\text{SiO}_2$ . This is comparable to the corrosion of vitreous silica in alkaline media.

Further potential is also given to the active-filler-controlled pyrolysis [1] of siloxane based ceramic precursors, where the free carbon phase plays an essential role as a reaction partner of the active filler compounds leading to the formation of, for example, metal carbides.

Finally, it has been shown that conclusions can be drawn from the lead oxide redox analysis of the ceramic residue about the composition of the siloxane resin used as raw material. However, more siloxane systems need to be investigated to enable the further development of raw materials and ceramic products.

The developments made in the field of poly(siloxane) derived ceramics and their composites make these materials attractive for wear and oxidation resistant coatings, sealants, fibres and matrix materials, especially for light weight constructions.

#### 4. Conclusions

The current work indicates that pyrolysis products of siloxane polymers, especially those of polymethylsiloxane, produced at  $1000^\circ\text{C}$  in vacuum are

amorphous or nanocrystalline composites of SiO<sub>2</sub>, SiC and C. This conclusion can be drawn from the experimental results of dilatometry and a new method of quantitative redox analysis with lead oxide. This new method enables the determination of the quantitative phase content of SiO<sub>2</sub>, SiC and C in siloxane derived ceramics, which allows the correlation of properties with composition, e.g. thermal/electrical conductivity, with free carbon content of the material. The results arising from this analysis could be useful for tailoring and engineering properties such as thermal expansion and refractoriness.

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