

STUDY ON PYROLYSIS OF POLYPHENYLSILSESQUIOXANE*

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Abstract X-ray photoelectron spectroscopy and Raman spectroscopy were used to determine the chemical change of polyphenylsilsesquioxane (PPSQ) during pyrolysis in flowing nitrogen. Two temperature ranges were found for pyrolysed PPSQ below and above 600°C, respectively. The former is related to the rearrangement of PPSQ backbone and the latter reflects that most of backbone structure of PPSQ might be broken down and unorganized. Carbon formed in carbonization of PPSQ sample pyrolysed at 900°C should be sp^3 bonded carbon with crystallite size effects or defects.

Keywords Pyrolysis, Polyphenylsilsesquioxane

INTRODUCTION

Polysilsesquioxanes can serve as easily synthesized precursors of silicon oxycarbides^[1]. In 1984, Chi and his associates first reported the conversion of silsesquioxanes to silicon oxycarbide, in which silicon, oxygen and carbon were incorporated into an amorphous network^[2, 3]. Ever since, the use of polysilsesquioxanes as precursors of silicon oxycarbide ceramics through pyrolysis at elevated temperatures in inert atmospheres has been a very active field of research. This group of materials has potential application as ceramic composite matrices and as coating and sealants for high-temperature materials^[1].

In polyphenylsilsesquioxane (PPSQ), the substituent on the silicon atom is a phenyl group, and it is generally characterized by its high thermal stability^[4]. Hurwitz studied the pyrolysis of polysilsesquioxanes synthesized by hydrolysis and condensation of phenyl and methyltrimethoxysilanes^[5]. Zhang and Shi investigated the pyrolysis of PPSQ by using gas chromatography (GC) and thermogravimetric analysis (TGA). Emphasis was placed on comparing the pyrolysis of PPSQ with that of copolymer of PPSQ with polydimethylsiloxane and polydiphenylsiloxane. The results showed that PPSQ decomposes by mechanisms of phenyl group elimination and carbonization^[6].

In this paper, the pyrolysis of PPSQ was further studied by means of X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Fourier transform-infrared spectroscopy (FT-IR). The result shows that the mechanism is more sophisticated than simple phenyl group elimination and carbonization.

EXPERIMENTAL

PPSQ was synthesized from phenyltrimethoxysilane by hydrolysis/condensation and the detailed procedure was described elsewhere^[7]. Pyrolysis was performed with finely ground solid PPSQ of about 2–5 g in weight under nitrogen atmosphere. The sample was filled in a carborundum crucible and placed in a carborundum tube furnace over which nitrogen flowed. The samples were heated up at a rate of 10 K/min to different pyrolysis

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temperatures. The obtained pyrolysed samples (brownish or blackish lumps or powders) were used in the following investigations.

TGA was conducted in flowing nitrogen ($30 \text{ cm}^3/\text{min}$) at a heating rate of 10 K/min using TGA-1000.

XPS spectra were recorded using ESCALAB 220I-XL XPS spectrometer with $\text{AlK}\alpha$ (1486.6 eV) as the excitation source. The analyzed area of the pyrolysed material had a width of about $150 \text{ }\mu\text{m}$ and a length of $150 \text{ }\mu\text{m}$. The X-ray source power is $15 \text{ kV} \times 20 \text{ mA}$. The analyses were performed, under a residual pressure of less than $5 \times 10^{-7} \text{ mbar}$, on pyrolysed material after heat-treatment at 400 , 600 and 900°C . Because all the testing materials were insulators, the charge effect was calibrated with contaminated carbon ($\text{C}1\text{s}$ peak at 284.6 eV).

Changes in the chemical structure of the coatings were identified by FT-IR and Raman spectroscopies. Lumps of the pyrolysed material were carefully polished to fine dust using diamond pastes. The FT-IR spectrum was recorded in transmission from 4000 to 400 cm^{-1} at 1 cm^{-1} resolution, using a Bruker Equinox 55 FT-IR/FRA 106 spectrometer. The Raman data were obtained with a Bruker FRA 106/S spectrometer. The Raman spectra were collected using a Dilor X-Y microspectrometer fitted with a Ge detector in flowing argon and the bandpass was 4 cm^{-1} . The laser excitation source was the $1.06 \text{ }\mu\text{m}$ line of a YAG laser, operated at 150 mW , in order to avoid heating of the films.

RESULTS AND DISCUSSION

The TGA curve of pyrolysed PPSQ sample is shown in Fig. 1. The initial decomposition temperature is around 600°C , higher than that of polymethylsilsequioxane^[8, 9]. It suggests that two important decomposing ranges exist in the material as temperature is increased, below and above 600°C . The former results in a weight loss of 7.1% . The first weight loss in this range should be attributed to the loss of low molecular weight cyclic PPSQ structures, the evolution of continued condensation of silanol and the reaction of methoxide groups. In spite of the pyrolysis, the sample remains colorless. Severe decomposition reactions take place at the end of the first range, which will gradually darken the sample. It results in a marked decrease in the PPSQ weight (30%), which should be attributed to the elimination of phenyl groups^[6].

XPS spectrum recorded at different stages of pyrolysis shows that all materials are made of silicon ($\text{Si } 2\text{s}$ and $\text{Si } 2\text{p}$ peaks), carbon ($\text{C } 1\text{s}$ peak) and oxygen ($\text{O } 1\text{s}$ peak). The center of $\text{Si } 2\text{p}$ peak, derived from the XPS data, is plotted against the pyrolysis temperature in Fig. 2. From room temperature to 600°C , no obvious change of $\text{Si } 2\text{p}$ bonding energy could be observed, implying most of the backbone structure of PPSQ is retained although phenyl group begins to eliminate at the end of the range. Above 600°C , however, a significant increase of $\text{Si } 2\text{p}$ bonding energy was found. This means that most of the backbone structure of PPSQ might be broken down and unorganized. These two temperature ranges correspond to the ranges proposed in TGA analysis. The bonding energy 103.5 eV of PPSQ pyrolysed at 900°C is very similar to that of silica^[10].

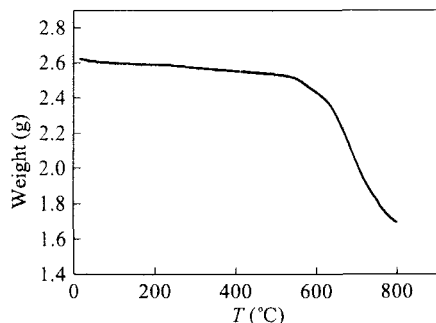


Fig. 1 TGA traces of PPSQ in N_2
Heating rate 10 K/min

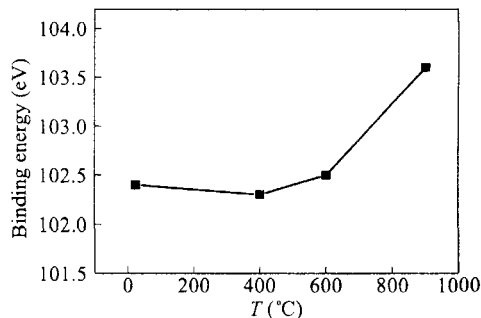


Fig. 2 Change of $\text{Si } 2\text{p}$ bonding energy of PPSQ pyrolysed at different temperatures

Elemental analysis of various samples of PPSQ pyrolysed at different temperatures, derived from the XPS peaks (recorded in the high-resolution mode), is plotted against heating temperature in Fig. 3. With increasing temperature carbon content decreases while silicon and oxygen contents increase, which could be due to the reaction of phenyl groups. Some phenyl groups are eliminated to form benzene molecules; some phenyl groups are carbonized^[6], which gradually darkened the sample; and some phenyl groups might react with silicon to form silicon oxycarbide.

During heating the powdery PPSQ from room temperature to 900 °C, some melt flow occurred, which turned PPSQ into a solid lump at the end of pyrolysis. One specimen was taken from the surface of the lump and the other from the core. Si 2*p* bonding energy (103.6 eV) of the surface specimen is slightly higher than that of the core specimen (103.4 eV). Elemental analyses of these two specimens, also derived from the XPS peaks (recorded in the high-resolution mode), are listed in Table 1. The carbon content of the surface sample is lower than that of the core sample, which might be attributed to the phenyl groups on the surface having more chances to escape.

Table 1. Elemental analysis of PPSQ pyrolysed at 900 °C

Sample	Carbon content (%)	Oxygen content (%)	Silicon content (%)
1(from the core)	53.8	26.9	19.2
2(from the surface)	49.9	29.3	20.8

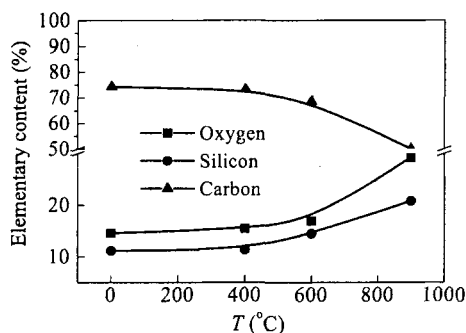


Fig. 3 Elemental analysis of PPSQ pyrolysed at different temperatures

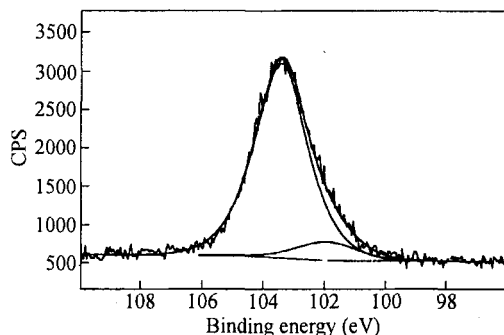


Fig. 4 Decomposition of Si 2*p* peaks of the XPS high-resolution spectra of PPSQ pyrolysed at 900 °C under nitrogen

XPS peak fitting is a useful tool to study multi-component materials. Since the peak positions of XPS data vary somewhat from instrument to instrument, an authentic sample of silica as a reference was run to confirm the peak position. The Si 2*p* bonding energy of silica is 103.1 eV, in a good agreement with literature^[10–14]. As shown in Fig. 4, an intense and broad peak of Si 2*p* bonding energy pyrolysed at 900 °C was observed and a small peak might exist at the right-bottom part of the broad peak. Based on the above observation, XPS peak fitting of the broad peak was conducted at 104.0 and 102.2 eV, respectively. The energy values corresponding to the various chemical bonds, derived from the XPS peaks (recorded in the high-resolution mode) are listed in Table 2. The peak at about 104.0 eV is assigned to Si—O bonds^[10], whereas the other at about 102.2 eV has been assigned to Si—O—C bonds similar to silicon oxycarbide^[9, 10]. XPS peak fitting result shows that about 91% of the pyrolysed product is silica and 9% is silicon oxycarbide.

Infrared spectra of the pyrolysed PPSQ heated in N₂ are shown in Fig. 5. The absorption bands of phenyl group are characterized by absorption bands of 1420 cm^{−1}, 1588 cm^{−1} and 3060 cm^{−1}. With the rise of pyrolysis temperature, the band intensity decreased and disappeared at about 600 °C, implying that phenyl groups decomposed by side group elimination. Typical polysilsesquioxane absorption bands at 1025 cm^{−1} and 1146 cm^{−1}

might correspond to the regularity of ladder-like polysilsesquioxane^[15]. Two temperature ranges were also found from room temperature to 600 °C and from 600 to 900 °C, respectively. Below 600 °C, the intensity of 1025 cm⁻¹ decreased and that of 1146 cm⁻¹ increased with increase of temperature. It could be explained that the pyrolysis leads to the rearrangement of PPSQ backbone. From 600 to 900 °C, the peak positions of these two peaks became closer and finally merged into a large absorption peak. This change could be explained by assuming that most of the backbone structure of PPSQ might be broken down and unorganized.

Table 2. Binding energies (eV) corresponding to different atomic bondings in various materials containing silicon

Materials	Si 2p			References
	Si(C, O) (III)	Si-O (II)	Si-C (I)	
Ex-PCS filament surface	102.2	103.2	101.1	[9]
bulk	101.9		100.8	[9]
CVD SiC		103.4	101.2	[13]
PPSQ surface pyrolysed at 900 °C	102.2	104.0		Present work

Although carbonization of PPSQ occurring during pyrolysis was observed by Zhang^[6], detailed analysis was not obtained until today. In this study, PPSQ samples were prepared by pyrolysis at 300, 600, 800 and 900 °C in flowing nitrogen and Raman spectroscopy was used to analyze free carbon more accurately in these materials. All spectra of PPSQ are listed in Fig. 6. The absorption bands at around 3062 cm⁻¹ and 1018 cm⁻¹ belong to the Ar-H vibrations of phenyl group and the band at 1588 cm⁻¹ are C=C vibration of phenyl groups. With the rise of pyrolysis temperature, the above three peaks all decreased and disappeared completely at 600 °C, implying the disappearance of phenyl group. This result is in good agreement with the above XPS and FT-IR analysis.

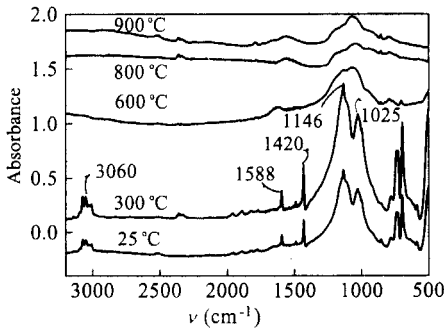


Fig. 5 FT-IR spectra of PPSQ pyrolysed at different temperatures

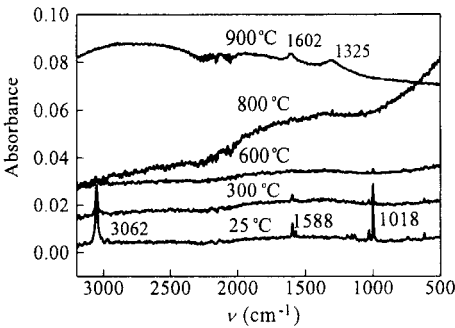


Fig. 6 Raman spectra of PPSQ pyrolysed at different temperatures

It was reported that the spectrum of microcrystalline graphite exhibits two bands, at well-defined energies of 1355 and 1580 cm⁻¹, the latter shifting to 1620 cm⁻¹ in nanocrystalline or turbostratic graphite, while both bands shift towards each other in amorphous carbon^[16]. PPSQ processed at 900 °C has a band at approximately 1325 cm⁻¹ that is a strong evidence for *sp*³ bonded carbon, a relatively large shift from the normal carbon A_{1g} band that appears around 1355 cm⁻¹. Amorphous *sp*³ carbon should have significant intensity at approximately 1300 cm⁻¹^[17]. As for the other absorption peak at 1580 cm⁻¹, the shift in frequency from the normal position at 1580 cm⁻¹ is manifestation of the relaxation of the wave vector conservation selection rule due to crystallite size effects or defects^[18, 19].

REFERENCES

- 1 Ma, J., Shi, L.H. and Xu, J., Chinese Polymer Bulletin, 2001, 55(5): 34
- 2 Chi, F.K., Ceram. Eng. Sci. Proc., 1983, 4: 704
- 3 Baney, R.H. and Chi, G.K., Europe Patent, 107,943
- 4 Ronald, H.B., Akihito, S. and Toshio, S., Chem. Rev., 1995, 95: 1409
- 5 Hurwitz, F.I., Heimann, P. and Farmer, S.C., J. Mater. Sci., 1993, 28: 6622
- 6 Zhang, X.S. and Shi, L.H., Chinese J. Poly. Sci., 1988, 20: 157
- 7 Ma, J., Xu, J. and Shi, L.H., Chinese Patent, 00130514. X
- 8 Ma, J., Shi, L.H. and Xu, J., Chinese Chemical Letters, 2002, 13(1): 75
- 9 Ma, J., Shi, L.H. and Xu, J., J. Appl. Polym. Sci., 2002, 85(5): 1077
- 10 Taylor, J. A., Appl. Surf. Sci., 1981, 7: 168
- 11 Bouillon, E., Mocaer, D. and Villeneuve, J. F., J. Mater. Sci., 1991, 26: 1517
- 12 Porte, L. and Sartre, A., J. Mater. Sci., 1989, 2: 271
- 13 Rahaman, M.N. and Dejonghe, L.C., Amer. Ceram. Soc. Bull., 1987, 66: 782
- 14 Mizokawa, Y., Geib, K.M. and Wilmsen, C.W., J. Vac. Technol. A., 1986, 4: 1696
- 15 Zhang, X.S. and Shi, L.H., Chinese J. Polym. Sci., 1987, 5: 359
- 16 Pivin, J.C. and Colombo, P., J. Mater. Sci., 1997, 32: 6163
- 17 Wada, N., Gaczi, P.J. and Solin, S.A., J. Non-Cryst. Solids., 1980, 35: 543
- 18 Knight, D.S. and White, W.B., J. Mater. Res., 1989, 4: 385
- 19 Nemanich, R.J. and Solin, S.A., Phys. Rev. B., 1979, 20: 392