

## Preliminary Study on Pyrolysis of Polymethylsilsesquioxane by FT-IR and XPS

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**Abstract:** Changes of composition and structure of various samples of polymethylsilsesquioxane (PMSQ) pyrolysed at different temperature under flowing nitrogen were investigated by means of FT-IR and X-ray photoelectron spectroscopy. Two temperature domains correspond to important changes in the chemical composition of PMSQ. The former ( $T_p < 500^\circ\text{C}$ ) is related to the transition from regular structure to irregular structure and the latter ( $T_p > 500^\circ\text{C}$ ) is associated with the organic-inorganic transition.

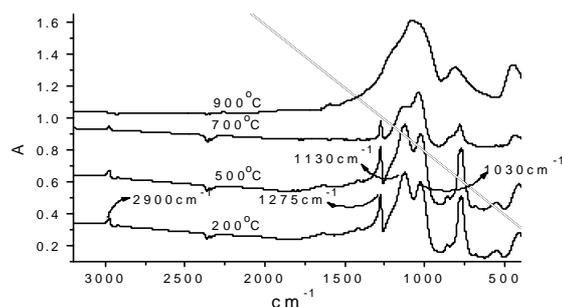
**Keywords:** Polymethylsilsesquioxane, pyrolysis, X-ray photoelectron spectroscopy.

The term polysilsesquioxanes in this paper refers to all structures with the empirical formulas  $(\text{RSiO}_{3/2})_n$  where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organo-functional derivatives of alkyl, alkylene, or aryl. Polymethylsilsesquioxane (PMSQ) is characterized by its low weight loss at high temperatures. X-ray photoelectron spectroscopy (XPS) characterization of PMSQ was unavailable from reported literatures. In this study, the pyrolysis was carried out in an inert atmosphere up to  $900^\circ\text{C}$ . The conversion process, intermediate and final products were characterized by FT-IR and X-ray photoelectron spectroscopy (XPS). PMSQ was synthesized from methyltrimethoxysilane by hydrolysis/condensation and then crosslinked in air at  $80^\circ\text{C}$  for 3 hours, as described elsewhere<sup>1</sup>.

Infrared spectra over the wavenumber range from 400 to  $4000\text{ cm}^{-1}$  of the pyrolysed PMSQ heated in  $\text{N}_2$  are shown in **Figure 1** (Perkin-Elmer System 2000 spectrometer). The absorption bands at around  $2900\text{ cm}^{-1}$  belong to the C-H vibrations of  $-\text{CH}$ ,  $-\text{CH}_2$ , and  $-\text{CH}_3$  groups. The methyl groups ( $\text{CH}_3$ ) are also characterized by absorption bands of  $1410\text{ cm}^{-1}$  and  $1275\text{ cm}^{-1}$ , respectively. The Si- $\text{CH}_3$  band intensity decreases with increasing heat-treatment temperature and its corresponding structure is decomposed around  $700^\circ\text{C}$  and disappeared completely at  $900^\circ\text{C}$ . Typical polysilsesquioxane absorption bands are at  $1030$  and  $1130\text{ cm}^{-1}$ , corresponded to the regularity of ladder-like polysilsesquioxane<sup>2</sup>. With increase of pyrolysis temperature, the band intensity of  $1130\text{ cm}^{-1}$  decreases, but the band intensity of  $1030\text{ cm}^{-1}$  increases.

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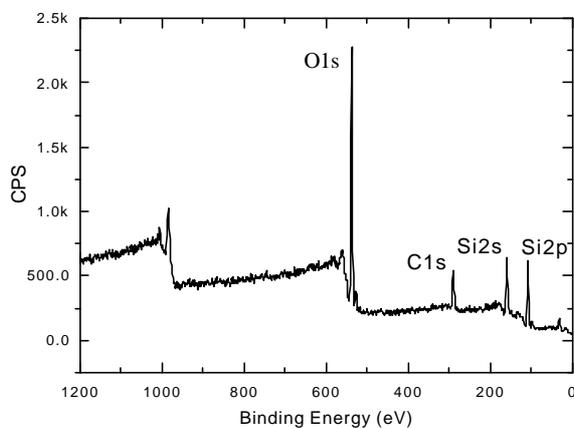
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**Figure 1** FT-IR spectroscopy of PMSQ heated at different temperature

It means the regularity of PMSQ decreases with increase of pyrolysis temperature. At 900°C, the two bands disappeared and a strong and large absorption band appeared at 1100  $\text{cm}^{-1}$ . This large band is similar to that of  $\text{SiO}_2^3$ . It seems that organic group gradually disappears with increasing temperature.

The XPS spectra were recorded (ESCALAB 220I-XL XPS spectrometer) with  $\text{AlK}\alpha$  (1486.6 eV) as the excitation source on the analyzed area of the pyrolysed material having a width of about 150  $\mu\text{m}$  and a length of 150  $\mu\text{m}$ . The X-ray source power is 15  $\text{kV}\times 20\text{ mA}$ . The analysis were performed under a residual pressure less than  $5\times 10^{-7}$  Pa after heat-treated at 200, 500, 700 and 900°C respectively in  $\text{N}_2$ . Because all the materials were insulators, the charge effect was calibrated with contaminated carbon (C 1s peak at 284.6 eV).

XPS analysis performed at different stages of pyrolysis shows all materials are made of silicon (Si2s and Si2p peaks), carbon (1s peak) and oxygen (O1s peak), as illustrated in **Figure 2**.

**Figure 2** XPS spectrum of PMSQ crosslinked in air and heated at 900°C under an inert atmosphere

The Si 2p peak consists of two or three components<sup>4-7</sup>. The peak at about 101 eV is assigned to Si-C bonds, whereas the peak at about 103eV has been assigned to Si-O bonds, which is similar to those present in silica<sup>4</sup>. Finally, the peak at about 104 eV for the polymeric materials that increases at first and then decreases as pyrolysis proceeds towards inorganic state. The signal observed between Si-C and Si-O bonds was assigned to the ternary Si (C, O) species. A similar component has also been reported<sup>5,6</sup>.

**Table 1** Binding energies (eV) corresponding to different atomic bonding in various materials containing silicon

Materials	Si (C, O) (III)	Si-O (II)	Si-C (I)	References
SiO-layer on silicon	102.2	103.2	101.1	4
Ex-PCS filament surface	102.2	103.2	101.1	5
bulk	101.9		100.8	6
CVD SiC		103.4	101.2	7
PMSQ surface pyrolysed at 900°C	102.3	103.5		Present work

XPS data recorded from pyrolysed PMSQ, crosslinked in air and heat-treated under an inert atmosphere at different temperatures, confirmed the complex chemical nature of ex-organosilicon precursor, which has been already mentioned by several researchers<sup>7,8,9,10</sup>. In order to ascertain assignments of the XPS peak components to chemical bonds, our data in **Table 1** are compared with data available from literature for silicon-based materials. The binding energies derived from component I of Si 2p peaks can be assigned to Si-C bonds. The binding energy, corresponding to component II of the Si 2p Si-O bonds, is similar to those mentioned for silica<sup>4</sup>. Finally, component III of the Si 2p was assigned to the ternary Si (C, O) species as already proposed by many researchers<sup>4,6,8,11</sup>.

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**.

**Table 2** Binding energies (eV) derived from the XPS peaks in heat treated PMSQ at different stages of pyrolysis

PMSQ treatment	Si2p		
	Si (C, O) (III)	Si-O (II)	Si-C (I)
At 200°C	102.4	103.3	101.3
At 500°C	102.5	103.5	101.3
At 700°C	102.4	103.3	
At 900°C	102.3	103.5	

A quantitative analysis of the chemical bonds in the materials at different steps of the PMSQ heat-treatment is given in **Table 3**. It shows that two temperature domains correspond to important changes in the chemical composition of the PMSQ: *i.e.*  $T_p < 500^\circ\text{C}$  and  $T_p > 500^\circ\text{C}$ . The former is related to the transition from regular structure to irregular structure and the latter is thought to be associated with the organic-inorganic transition. From room temperature to  $500^\circ\text{C}$ , the values of Si-O and Si-C bonds decrease, but that of Si (C, O) increases.

**Table 3** Quantitative XPS analysis of the chemical bonds (at.%) at different stages of pyrolysis

Materials	Si2p		
	Si (C,O) (III)	Si-O (II)	Si-C (I)
At 200°C	60.1	21.5	18.3
At 500°C	71.9	13.2	14.8
At 700°C	10.6	89.3	
At 900°C	8.3	91.6	

According to FT-IR result, the regularity of PMSQ decreases at that temperature interval. Therefore, the change of the values of Si-O, Si-C and Si (C, O) bonds means the decrease of the regularity of PMSQ. During the organic-inorganic transition at 500-900°C, the percentage of Si-O bond increases magnificently, but the value of Si (C, O) decreases excessively. It proves that the main component of the final pyrolysed product is SiO<sub>2</sub>. The data also show that the materials heat-treated at 700 and 900°C are almost free of Si-C.

### Acknowledgments

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### References

1. J. Ma, J. Xu, Chinese Patent 130, 514. X, **2000**.
2. Z. S. Xie, Z. Q. He, X. R. Dai, R. B. Zhang, *Chinese J. Polym. Sci.*, **1989**, 7 (2): 183.
3. *Atlas of Polymer and Plastics Analysis*, 2nd. Federal Republic of Germany, **1980**, 3.
4. J. A. Taylor, *Appl. Surf. Sci.*, **1981**, 7, 168.
5. E. Bouillon, D. Mocaer, J. F. Villeneuve, *J. Mater. Sci.*, **1991**, 26, 1517.
6. L. Porte, A. Sartre, *J. Mater. Sci.*, **1989**, 2, 271.
7. Y. Mizokawa, K. M. Geib, C. W. Wilmsed, *J. Vac. Technol. A.*, **1986**, 4, 1696.
8. J. Lipowitz, H. A. Freeman, R. T. Chen, E. R. Prack, *Adv. Ceram. Mater.*, **1987**, 2, 121.
9. C. Laffon, A. M. Flank, R. Hagege, P. Olry, J. Cotteret, *J. Mater. Sci.*, **1989**, 24, 1503.
10. C. D. Wager, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation Physical Electronics Division 6509 Flying Cloud Drive Eden Prairie, Minnesota, **1979**, Part 52.
11. L. C. Aswyer, R. T. Chen, F. Haimback, P. J. Harget, *Ceram. Engng. Sci. Proc.*, **1986**, 7, 914.

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