

Mechanism of Curing Process for Polycarbosilane Fiber with Cyclohexene Vapor

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ABSTRACT: The reaction process of polycarbosilane (PCS) fiber cured by cyclohexene vapor has been studied and compared with that of PCS fiber cured by air. The influence of curing temperature on Si—H bond reaction degree and gel content, the structure and composition of PCS were investigated by FTIR, EA, TGA, NMR, and GC-MS. The results showed that, Si—H bond in the molecular structure of PCS reacted during cyclohexene curing process and the reaction degree increased when the curing temperature increases. Simultaneously, gel content of PCS fiber rapidly increased till PCS fiber became infusible. Si—H radical and

Si—CH₂ radicals formed Si—CH₂—Si crosslinking of PCS molecules through the agency of cyclohexene. Some cyclohexyls linked to principal chain of PCS, which was proven by ¹³C-CPMAS-NMR, and broke off, and cyclohexane and some monosilane are generated as byproducts when temperature increased. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1651–1657, 2007

Key words: polycarbosilane; cyclohexene; chemical vapor curing; SiC fiber

INTRODUCTION

Silicon carbide (SiC) ceramic fibers, which are well known for their excellent tensile strength, thermal shock resistance, and intermiscibilities with many matrices, are applied widely in materials engineering of high performance composites. In recent years, the method of pyrolysis of an organic precursor to prepare SiC fibers has attracted considerable attention and is widely studied. The method includes the synthesis of polycarbosilane (PCS) precursor, melt spinning, fiber curing, and heat treatment at high temperature. During the curing process, the polycondensation and crosslinking reaction of PCS molecule take place; PCS fiber becomes indissoluble and infusible, and remains fiber shape which is to be treated at high temperature.^{1,2}

The common curing method for PCS fiber, air oxidation, introduces much oxygen into the fibers and forms SiC_xO_y phase, which is unstable at high temperature and decomposes to β-SiC crystals by evolving SiO and CO, which causes loss of fiber strength. And traces of oxygen and water in the carrier gas form surface defects of SiC fibers, such as oxide film and pits/splits. The oxidation rate of SiC increases 20 times especially when oxygen and water coexist.^{3–8}

Therefore, most recent work is devoted to the lowering of the oxygen content in the fibers, such as elec-

tron beam(EB)/γ-ray radiation, chemical vapor curing (CVC), and dry spinning of high molecular weight PCS.^{9–12} Compared with others, CVC method selects nonoxygen active reactants (cyclohexene, 1-octylene, etc.) vapors to cure green fibers, which is feasible and suit for industrialization. And the SiC fiber prepared has low oxygen content (<0.5 wt %), enduring 1400°C with acceptable strength residual.^{13,14} Although the method has been successfully used to fabricate low oxygen content SiC fibers, the mechanism of CVC is still unclear and the research is insufficient. Hasegawa, the CVC method inventor, assumed the reaction of PCS with cyclohexene to be a free radical reaction.¹³ But there are still some important problems, as the evolution of radicals, the formation of crosslinking structures, and the role of cyclohexene in reactions, etc., to explore. Besides, further experimental evidence is required to substantiate and enrich the concept presented above. The mechanism research can also give some directions in finding some more effective curing vapor and method. On the basis of extensive research and experimental results of CVC reaction, we presented a new and detailed mechanism of PCS fiber with cyclohexene.

EXPERIMENTAL

Materials and experimental details

Cyclohexene was purchased from Shanghai Chemical Plant (Shanghai, China). High-purity gas N₂ (99.999%) was purchased from Jingxiang Gas Plant

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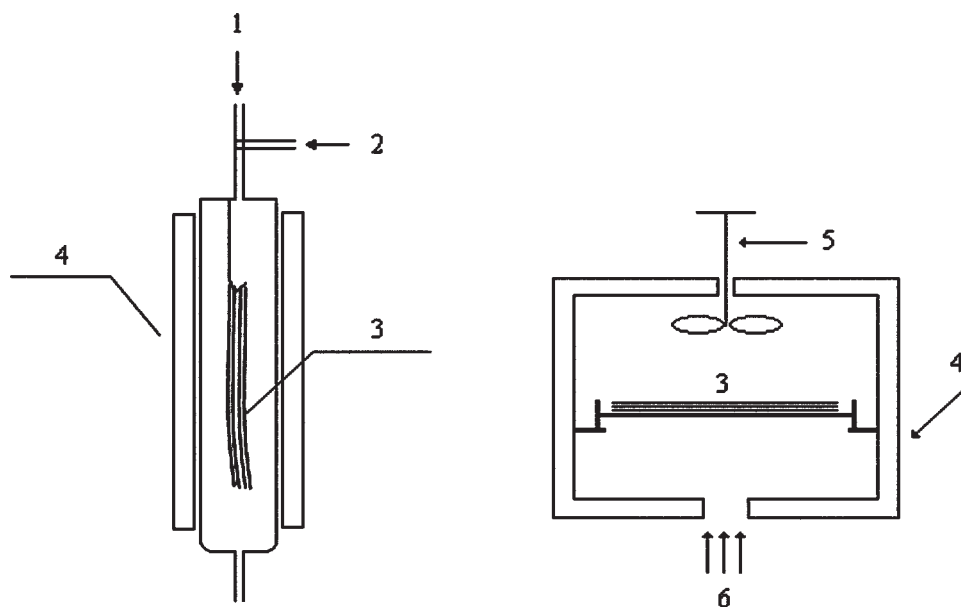


Figure 1 Schematic diagrams of CVC apparatus and air oxidation equipment for PCS green fibers: (1) Cyclohexene vapor, (2) N_2 , (3) PCS fiber, (4) electric furnace, (5) suction ventilating fan, and (6) fresh air inlet.

(Changsha, China). The softening points of polycarbosilane (PCS) green fibers range from 190°C to 230°C.

Some PCS green fibers were heated in the cyclohexene atmosphere to specific temperatures ranging from 100°C to 400°C, and then cooled naturally to the ambient temperature. Some PCS green fibers were heated in fresh air from 100°C to 250°C. Schematic diagram of chemical vapor curing (CVC) apparatus and air oxidation equipment is shown in Figure 1.

Measurements

Uncured PCS fiber, cyclohexene cured PCS fiber (sampling at 250°C), and air oxidized PCS fiber (sampling at 250°C) were ground with KBr powder and compressed to tablets for the FTIR analysis. Fourier transform infrared (FTIR) spectra were obtained with a Nicolet-360 IR spectrometer in the wave-number range of 4000–400 cm^{-1} with standard procedures. Si–H bond content of PCS fiber was calculated from the absorbency ratio of characteristic absorption peaks at 2100 cm^{-1} and 1250 cm^{-1} A_{Si-H}/A_{Si-CH_3} . Si–H bond reaction degree of PCS fiber (P_{Si-H}) was calculated by the following formula^{2,6}:

$$P_{Si-H} (\%) = \frac{(A_{Si-H}/A_{Si-CH_3})_{original} - (A_{Si-H}/A_{Si-CH_3})_{cured}}{(A_{Si-H}/A_{Si-CH_3})_{original}} \times 100 (\%) \quad (1)$$

A_{Si-H} , the absorbency of Si–H absorption peak; A_{Si-CH_3} , the absorbency of Si– CH_3 absorption

peak; original, uncured PCS fiber; cured, cured PCS fiber.

The thermoanalysis (TG-DTA, a WRT-1 Thermal Analyser, Shanghai) was carried out via heating the PCS powder from 130°C to 250°C in a 40 mL/min cyclohexene/ N_2 (carrying gas) mixing flow to analyze the thermal behavior of PCS reacting with cyclohexene, and 250 to 350°C in a 40 mL/min N_2 flow to observe the pyrolysis of PCS in thermal curing, both at the heating rate of 5°C/min.

The elemental contents were analyzed instrumentally at the National Key Laboratory of Powder Metallurgy of China. The Si, C atoms contents in the samples were measured by the CS-444 Carbon/Sulfur analyzer and GB 4333.1-84 method. Gel content was measured with Soxhlet extraction apparatus. Cyclohexene cured PCS fibers (sampling from 100°C to 400°C) and air oxidized PCS fibers (sampling from 100°C to 250°C) were extracted 20 times with xylene as solvent. The ^{13}C CPMAS NMR spectra and ^{29}Si MAS NMR spectra of PCS fiber cured by cyclohexene and air (to 250°C) were obtained using a Bruker AV 300 spectrometer, operating at 4.5 KHz. The GC-MS analyses of the gaseous product of CVC reaction were carried out by a HP-6890/5973 GC/MS instrument.

RESULTS AND DISCUSSION

FTIR spectroscopy

Figure 2 overlaps the representative IR spectra of the PCS cured by cyclohexene (sampling at 250°C) with the ones of uncured fibers and air cured fibers (sam-

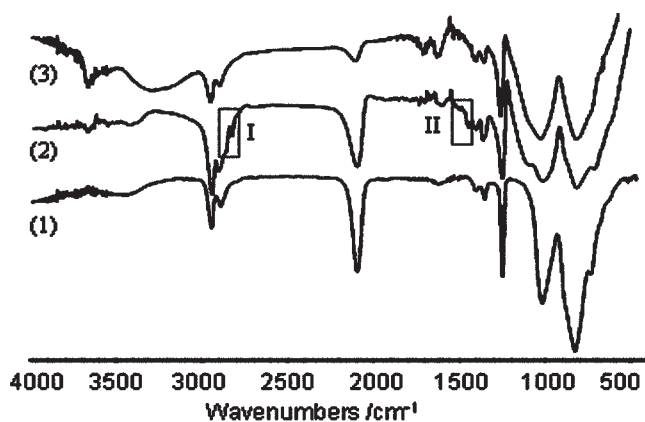


Figure 2 Fourier transform infrared spectra of PCS fibers: (1) uncured PCS fiber; (2) PCS fiber cured by cyclohexene to 250°C; (3) PCS fiber cured by air to 250°C.

pling at 250°C) to give a clear comparison. As shown in the spectrum, cyclohexene mainly consumed the Si—H bonds of the PCS, which led to the apparent degradation of the peak at 2100 cm^{-1} . This is the same as that of the air cured PCS.

Furthermore, some new absorbing peaks not belonging to the uncured fibers appeared on the spectra of cyclohexene cured PCS, as shown in the regions marked I and II of Figure 2. There are a small shoulder peak and a side peak at 2880 and 2838 cm^{-1} , respectively, shifting from the C—H stretching vibration peak (2900 cm^{-1} , 2950 cm^{-1}). Besides the C—H bending vibration peaks of Si—CH₃ (1400 cm^{-1}) and Si—CH₂—Si (1360 cm^{-1}) in PCS, two weak peaks appear at 1376 cm^{-1} , 1456 cm^{-1} , respectively, which do not belong to uncured PCS fiber either.

Compared with the IR spectrum of cyclohexene cured PCS with the spectra of pure cyclohexene and cyclohexane, it was found that the new peaks (at 2880, 2838 cm^{-1} , 1376 cm^{-1} and 1456 cm^{-1} , respectively) was assigned to the new structures formed during the reaction of PCS and cyclohexene. And these structures were possibly cyclohexyls bonded with the PCS molecules, which should be further confirmed.

Gel content and Si—H reaction degree

Influence of temperature on the Si—H reaction degree of the PCS fiber by CVC and air oxidation method is shown in Figure 3. It shows that the Si—H reaction degree increased linearly with temperature either in cyclohexene vapor or in air. But the rate of increase was different from each other. Obviously, Si—H bonds had a better reaction activity with oxygen than with cyclohexene.

Figure 4 shows the effect of Si—H reaction degree on gel content of PCS fiber cured by two methods. The gel content of the PCS fiber was gradually

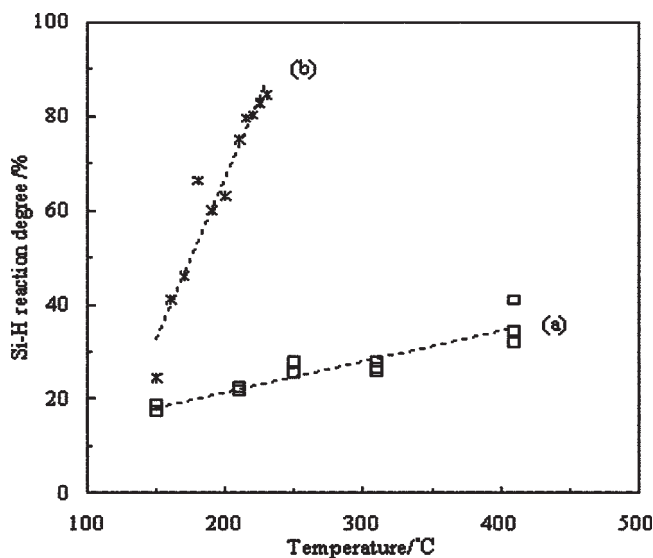


Figure 3 Effect of curing temperature on Si—H reaction degree (a) cyclohexene cured; (b) air cured.

increased with the increasing of Si—H bond reaction degree, until the PCS fiber became infusible. Commonly, when gel content increases to 80%, PCS fiber will not melt and remains of the fiber shape is to be treated at high temperature in the pyrolysis process.^{2,6} Table I shows the different gelation conditions of two curing methods. The data indicate that Si—H bonds have more side reactions with oxygen than with cyclohexene, which have no contribution to the crosslinking of PCS. So air oxidized PCS fiber has a higher Si—H consumption than CVC fiber. This was probably due to the difference between their reaction mechanisms. When PCS green fiber was cured in air,

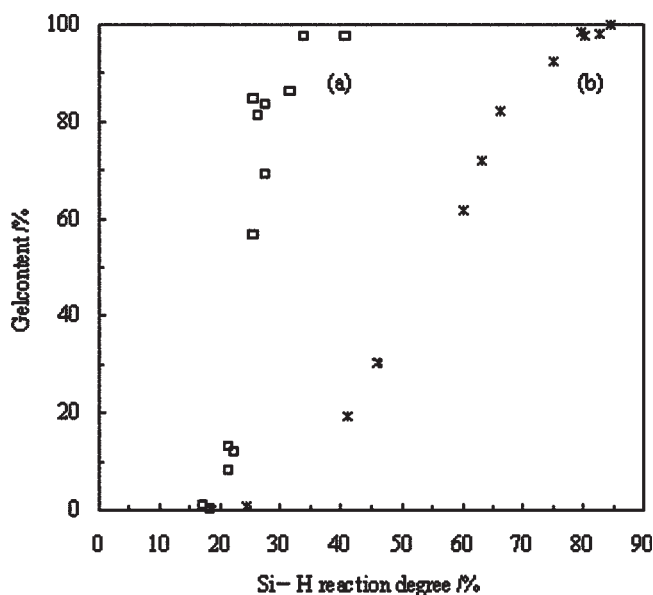
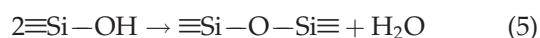
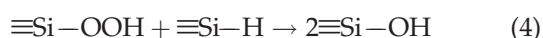
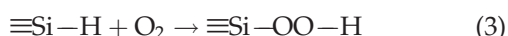


Figure 4 Effect of Si—H reaction degree on gel content in PCS fibers (a) cyclohexene cured; (b) air cured.

TABLE I
Gelation Condition of PCS Fiber: $(P_{\text{Si-H}})_{\text{gel}}$: $P_{\text{Si-H}}$ when gel weight content of PCS begins to increase rapidly;
 $(P_{\text{Si-H}})_{\text{gel}>80\%}$: $P_{\text{Si-H}}$ when gel weight content of PCS begin to exceed 80%

Curing condition	$(P_{\text{Si-H}})_{\text{gel}}$ (%)	$(P_{\text{Si-H}})_{\text{gel}>80\%}$ (%)
Air	40	65
Cyclohexene	22–26	28–32

a large number of Si—H bonds were oxidized to produced Si—OH bonds. Some of the Si—OH bonds formed the structure of Si—O—Si bonds; others remained and had no contribution to the crosslinking reaction. The formula of the reaction between PCS and oxygen was presented as following.^{2,6}



Mechanism of the reaction between PCS and cyclohexene was totally different from that of PCS oxidation, and we would discuss it later.

Thermoanalysis

Figure 5 indicates the thermal behavior of PCS reacting with cyclohexene at different temperatures. As shown in the curve, there was no obvious exothermic peaks appearing until the temperature reached 180°C. Above 180°C, a drastic exothermic status occurred with the temperature increasing. When the cyclohexene shuts down at 250°C, the exotherm reached maxi-

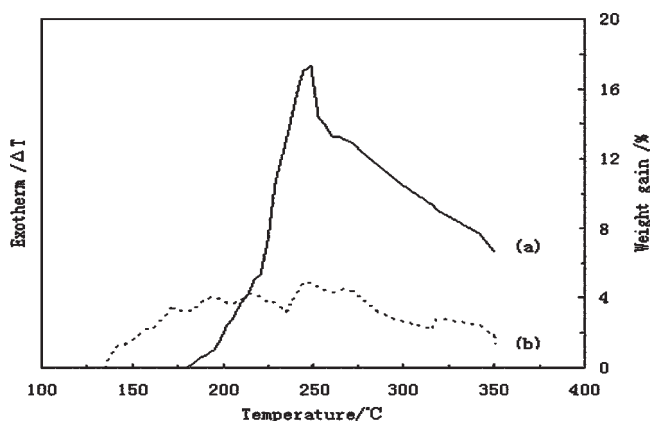


Figure 5 TG-DTA curve of PCS (a) exotherm, (b) weight gain.

TABLE II
Element Composition of PCS Fibers

Sample	Conditions	Composition (wt %)			C/Si (at.)	O/Si (at.)
		Si	C	O		
A	Uncured PCS fiber	49.4	40.2	1.6	1.90	0.06
B	Cyclohexene cured to 250°C	45.9	41.4	5.1	2.10	0.19
C	Air oxidized to 250°C	42.7	30.2	15.2	1.65	0.62

um level and then decreased rapidly till 350°C. Correspondingly, the weight gain did not happen until 180°C, and increased continuously and steadily till 250°C. Over 250°C, Weight loss happened for the reason of thermal curing. These results exhibit that the reaction between PCS and cyclohexene is a typical exothermic one and causes weight gain of PCS. The weight gain of PCS oxidation begins at the temperature of 160°C,^{2,6} which is lower than that of cyclohexene curing (180°C). It indicates that the reaction between PCS and cyclohexene is much harder to occur and needs more energy to induce.

Elemental analysis

Table II shows the chemical composition of uncured PCS fiber, CVC fiber, and air oxidized PCS fiber (both cured to 250°C). Compared with air oxidized fiber, CVC fiber contained much less oxygen and much more carbon. The atomic ratio of C to Si of PCS fiber increased after cyclohexene vapor curing process. It indicated that some carbonaceous structure bonded to the PCS molecules after the CVC reaction. This also tallies with the new peaks in FTIR spectra shown in Figure 2 and the weight gain of fibers indicated in Figure 5. Air oxidized fiber has

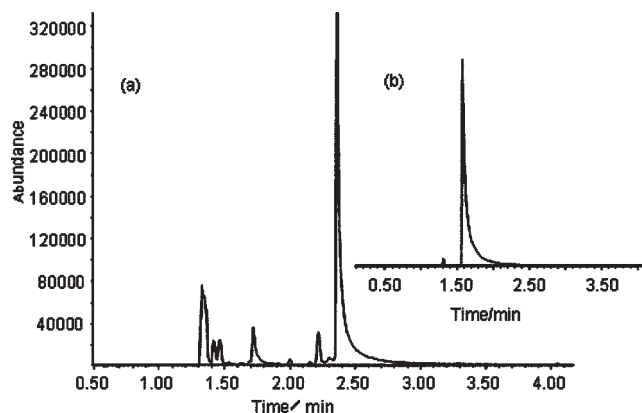


Figure 6 Gas chromatograms of gaseous product of CVC reaction and pure cyclohexene: (a) cyclohexene with PCS; (b) pure cyclohexene.

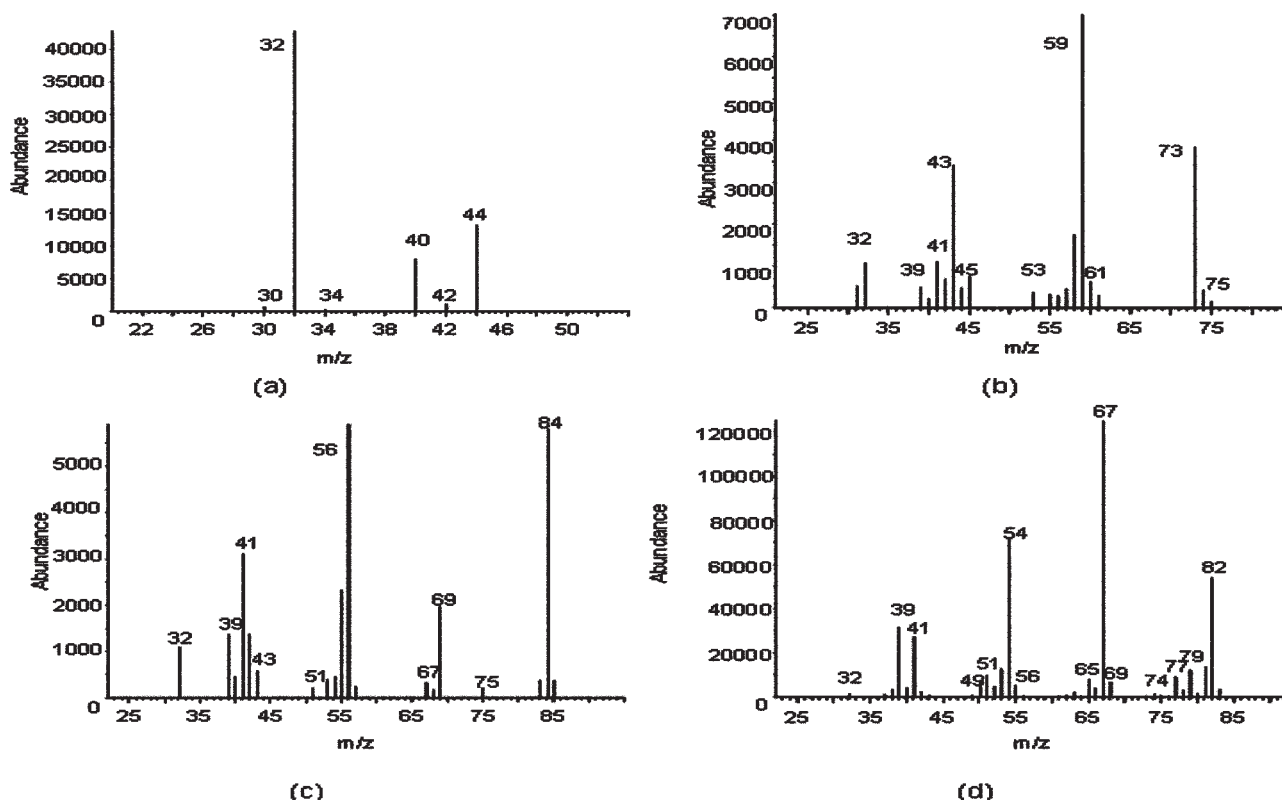


Figure 7 Mass spectra of gaseous product of CVC reaction: (a) $t = 1.360$ min, (b) $t = 1.431 \sim 1.740$ min, (c) $t = 2.238$ min, (d) $t = 2.411$ min.

much more oxygen and less carbon than CVC fiber, so the ratio of C/Si decrease so much.

GC-MS of the gaseous product of CVC reaction

The gas chromatographic and mass spectrum analysis (GC-MS) of the gaseous product of CVC reaction was carried out. The reaction temperature was 250°C . And the GC-MS spectra of gaseous product of CVC and pure cyclohexene at 250°C are both shown in Figures 6 and 7. At the time of 1.431 min, 1.478 min, 1.740 min, and 2.411 min there were several different chemicals being separated. ($T = 1.360$ min was CO_2 , brought by the instrument, was not the gaseous product of CVC). In the mass spectrums, nucleon number was 73, 84, and 82. The component of 73 included the segment of 31, 45, and 59, which were the typical fragment ions of $\text{C}_n\text{H}_{2n+3}\text{Si}$. It indicates that monosilane was the byproduct of CVC reaction. The components of 84 and 82 proved the existence of cyclohexane and cyclohexene. These findings of the experiment lead to the conclusion that cyclohexane and monosilane are the products of reaction between PCS and cyclohexene.

Solid state ^{13}C and ^{29}Si -NMR spectroscopy

The solid state ^{13}C -NMR spectra of the PCS fibers uncured, cured by cyclohexene vapor, and cured by

air (both cured to the temperature of 250°C), obtained by the cross-polarization/magic angle spinning (CP/MAS) technique is shown in Figure 8. The solid state ^{29}Si -NMR spectra obtained by the magic angle spinning (MAS) technique are shown in Figure 9.

In the ^{13}C spectrum (Fig. 8) of cyclohexene cured PCS fiber, the main peak at +3 ppm indicated carbon atoms bonded to silicon. This peak was probably due to superimposed $\text{Si}-\text{CH}_3$ and $\text{Si}-\text{CH}_2$ groups because the chemical shift difference between

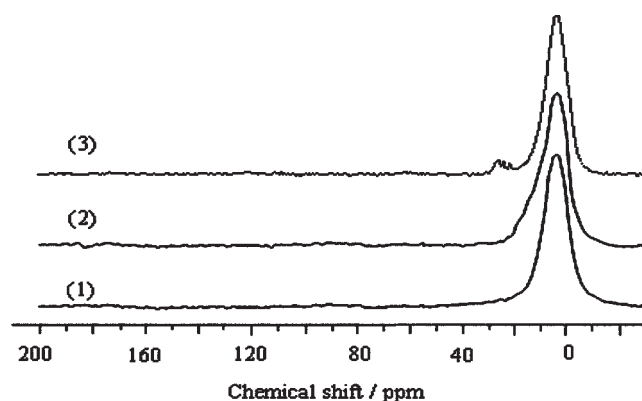


Figure 8 ^{13}C CPMAS NMR spectra of PCS fibers: (1) uncured PCS fiber; (2) PCS fiber cured by air to 250°C ; (3) PCS fiber cured by cyclohexene to 250°C .

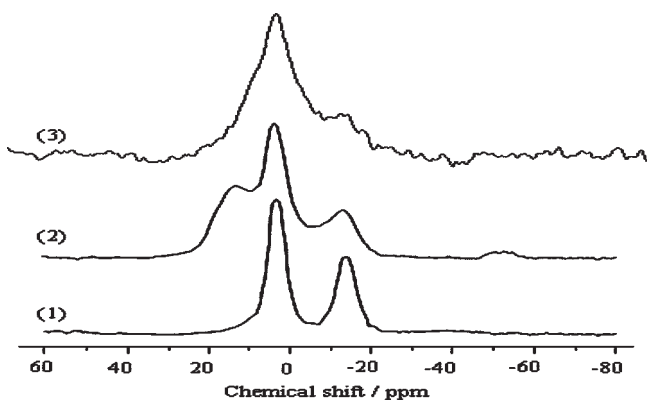


Figure 9 ^{29}Si MAS NMR spectra of PCS fibers: (1) uncured PCS fiber; (2) PCS fiber cured by air to 250°C ; (3) PCS fiber cured by cyclohexene to 250°C .

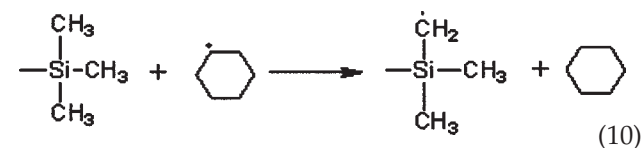
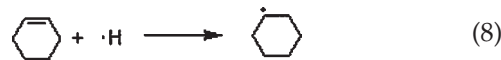
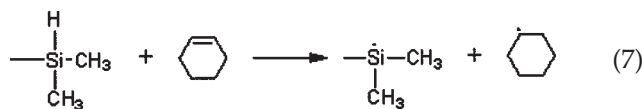
these two carbon environments is very small.⁷ The weak signal at around +25 ppm was assigned to the resonance of saturated hydrocarbon, which was not observed in the ^{13}C spectrum of uncured and air oxidized PCS fibers.⁷ These results exhibit that some new structure were formed during the reaction of PCS and cyclohexene. In these CVC conditions, ring cleavage reaction of cyclohexane could never happen.¹⁵ On basis of the chemical shift, it was clear that these structures were cyclohexyls bonded with the PCS molecules. Some cyclohexyls broke off from PCS molecular chain because of steric effect when temperature was increased. That was proved by GC-MS analysis of the gaseous product of CVC reaction.

In the ^{13}Si spectrum (Fig. 9), the signal at the chemical shift of around 0 ppm was assigned to the resonance of silicon bonded to four carbons (SiC_4). The signal at -18 ppm was assigned to silicon bonded to a hydrogen and three carbons (SiC_3H).⁷ From peak integrals, the ratio of SiC_3H to SiC_4 units was found to be about 0.39 : 1, and it was much less than the ratio 0.92 : 1 of uncured PCS fiber.² This indicates a crosslinking reaction of PCS molecules. And the ^{13}Si spectrum of cyclohexene cured PCS fiber had no signal at the chemical shift of around +15 ppm and -50 ppm, which belonged to $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{C}$.

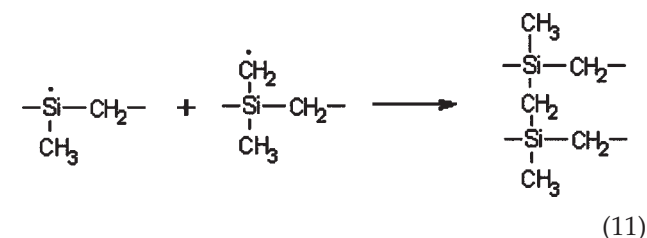
Mechanism of the reaction between PCS and cyclohexene

The experimental results of CVC indicate that the reaction between PCS and cyclohexene is a typical radical style. Free radicals are generated by the reaction between PCS and cyclohexene when temperature increases. And these radicals decrease the bond cleavage energies of PCS and initiate $\equiv\text{SiH}$ and $\equiv\text{SiCH}_3$ into radicals. Although it is less active in comparison with oxygen, the presence of cyclohexene could facilitate the radical formation, because it is very hard for $\text{Si}-\text{H}$ bond to break in an inert

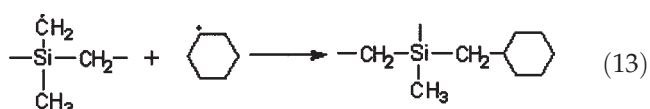
atmosphere at a low temperature.^{2,6} The reaction is demonstrated as following:



When temperature increases, $\equiv\text{Si}$ radicals combined with $\equiv\text{SiCH}_2$ radicals and formed the crosslinking bridges $\text{Si}-\text{CH}_2-\text{Si}$ among single PCS molecules. When the crosslinking reached some level, a three-dimension network was accomplished, resulting in cured PCS.



Owing to the predominant amount of cyclohexene, parts of newly formed radicals attack the unsaturated carbons, and introduce the ring of cyclohexyl into PCS. It has been observed in the IR spectra, EA results, and NMR spectra described above.



During the reaction, some $\equiv\text{SiCH}_2$ radicals combined with protons and became monosilane, which vented with the carrier gas. Because of the steric repulsive effects, some cyclohexyl broke off from the

PCS chain with the increasing of temperature. The results of GC/MS analysis of the gaseous product of CVC reaction had proved the existence of monosilane and cyclohexane.

CONCLUSIONS

The reaction between PCS and cyclohexene is an exothermic one, accompanied by weight gain, and proceed through free radical evolution route. Although less active than oxygen and requires higher temperature to react, cyclohexene induces the cleavage of $\equiv\text{SiH}$ and $\equiv\text{SiCH}_3$ in PCS to form radicals, transmits radicals and makes the reaction proceed successively. With the combination of these free radicals, crosslinking level of PCS molecules increases steadily, three-dimension network comes into being and PCS becomes infusible and insoluble. The ring of cyclohexyl is introduced into PCS and brings the variations in IR spectra, NMR spectra, weight gain, and carbon contents increase of PCS. Cyclohexane and monosilane are the byproducts of the reaction between PCS and cyclohexene. Further

research in the effect of cyclohexene on the composition and properties of SiC fibers is deserved.

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