

Synthesis of Polyaluminocarbosilane and Reaction Mechanism Study

FENG CAO,¹ DONG-PYO KIM,² XIAO-DONG LI,¹ CHUN-XIANG FENG,¹ YONG-CAI SONG¹

¹ Key Lab of C.F.C, National University of Defense Technology, Changsha, 410073, People's Republic of China

² Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Taejeon, 305-764, Korea

Received 4 May 2001; accepted 12 November 2001

ABSTRACT: Polyaluminocarbosilane (PACS) as the precursor of high-temperature resistant SiC fibers was synthesized by reacting polycarbosilane (PCS) with aluminum(III)acetylacetonate [Al(AcAc)₃] at 310°C in N₂ under ambient pressure. The reaction mechanism and the structure of PACS were investigated in detail by FTIR, GPC, GC/MS, ESCA, and elemental analysis. The reaction was proven complex involving the formation of Si—O—Al and Si—Al—Si bonds, which were accompanied by the evolution of 3-methoxy-2,2-dimethyl-oxirane, 2,3-dihydro-[1,4]dioxine, pent-3-en-2-one, and 3-ethyl-but-3-en-2-one, and acetylacetone. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2787–2792, 2002

Key words: synthesis; polyaluminocarbosilane; aluminum(III)acetylacetonate; polycarbosilane; reaction mechanism

INTRODUCTION

It is well known that polycarbosilane (PCS)-derived SiC-based fiber is a typical candidate for the high-temperature stable inorganic reinforcement of ceramic matrix composites (CMCs), but unfortunately, common PCS-derived SiC fiber is prone to degradation over 1200°C due to excess C, a high content of oxygen, and granular crystalline growth.¹ To achieve the high-temperature stability required of PCS-derived SiC fibers, heteroelements were incorporated into PCS as sintering aids and crystallization inhibitors at high temperature. Ishikawa et al.² prepared Zr containing SiC fiber via polyzirconocarbosilane synthesized

by reaction between PCS and zirconium acetylacetonate. The obtained fiber showed high tensile strength at high temperature due to the inhibition of crystalline β -SiC grain growth by the Zr. An alternative approach used Al containing PCS, for a similar purpose, by reaction between PCS and Al(OR)₃. Sorarù et al.³ prepared Si—Al—O—C fiber by pyrolyzing green polyaluminocarbosilane (PACS) fiber obtained from a reaction between PCS and Al(OBu^s)₂(etac). Another significantly stable Al containing SiC fiber was later reported by utilizing a similar precursor obtained by reaction between PCS and aluminum(II)acetylacetonate.⁴ A superhigh temperature-resistant fiber was produced by a procedure analogous to that used for Nicalon except for the incorporation of Al and the final sintering at 1800°C.

However, in other related reports, the synthesis and structure of PACS was only described briefly.⁴ In this study, the PACS synthetic procedure and its reaction mechanism are described in

Correspondence to: X.-d. Li (youlucky2000@yahoo.com).
Contract grant sponsor: Chinese Natural Science Fund; contract grant number: 59972042.

Contract grant sponsor: Korea Science and Engineering Foundation; contract grant number: 2000-2-30700-007-3.

Journal of Applied Polymer Science, Vol. 85, 2787–2792 (2002)
© 2002 Wiley Periodicals, Inc.

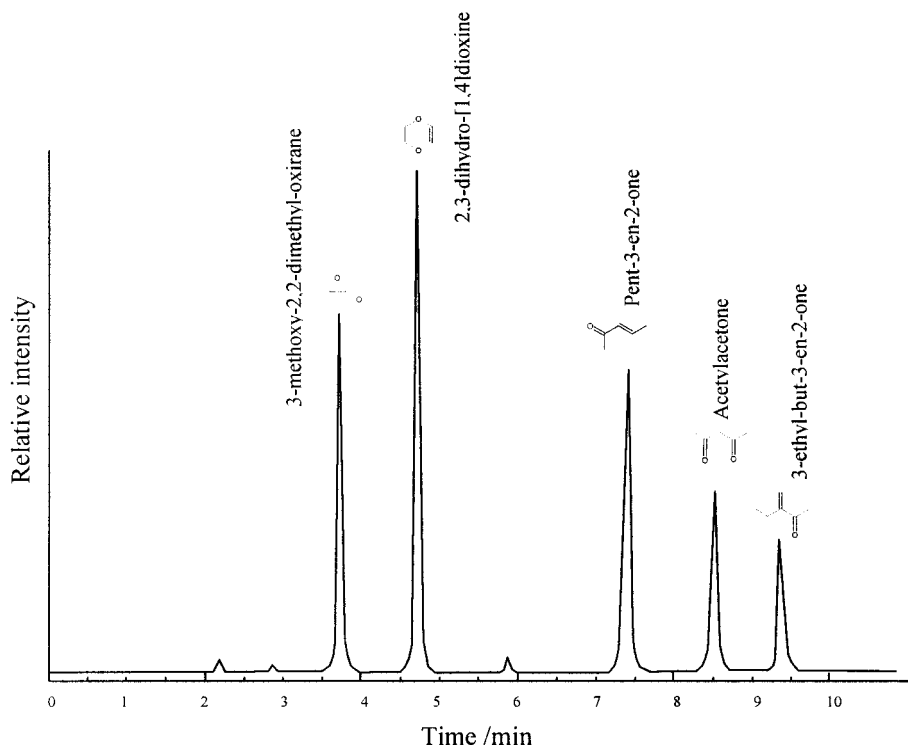


Figure 1 The gas chromatograms of liquid byproducts of the reaction between $\text{Al}(\text{AcAc})_3$ and PCS (weight ratio 1/2.33) at 310°C in nitrogen.

detail after thoroughly analyzing PACS and its byproducts. Furthermore, we found a novel reaction mechanism. The related SiC fiber product will be reported on in a separate article.

EXPERIMENTAL

PCS with a melting point of 200–210°C was synthesized by thermolysis of polydimethylsilane (PDMS), provided by the Xing Huo Chemical Plant, at 480–550°C and ambient pressure. PACS with various Al contents was synthesized with different weight ratios of $\text{Al}(\text{AcAc})_3/\text{PCS}$ (1/19, 1/9, 1/4, and 1/2.33). In a typical reaction, a 100-mL three-necked, round-bottom flask was equipped with a thermometer, a trap for volatile byproducts, and a refluxing condenser connected to a line adapter for nitrogen and vacuum. A fine powder mixture of PCS and $\text{Al}(\text{AcAc})_3$ (Aldrich, 99%) was charged into the flask; air was evacuated, and the system was filled with a nitrogen stream. The flask was heated to 310°C at a rate of 10°C/min and then held for 1 h. Volatile pale yellow by-products condensed in the cold trap during the reaction period. The residue in the

flask was solid PACS product, which became browner by increasing the $\text{Al}(\text{AcAc})_3/\text{PCS}$ ratio.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-360 spectrometer. PACS and the original PCS were analyzed in KBr pellets. Gas chromatography/mass spectroscopy (GC/MS) spectra were recorded by using a Shimadzu GC-17A, QP-5000 (Japan) equipped with a silica capillary column (30 m \times 0.25 mm). The system was operated by using class-5000 software, which provides complete control of the gas chromatograph, mass spectrometer, and autosampler from a computer operating in the Windows environment. The oven temperature was set at 50°C for 2 min prior to injection, programmed to 280°C at the rate of 10°C/min, and held at 280°C for 20 min. Helium was used as the carrier gas (head pressure, 20 kPa; total flow rate, 50 mL/min). The mass spectrometer was connected with GC and operated under electron-impact (EI) mode at an ionization energy of 70 eV. The molecular structures of the compounds separated by GC were determined automatically from a database.

Molecular weight distributions were determined by gel permeation chromatography by us-

ing a Waters-244 analyzer and s-Styragel columns calibrated with polystyrene standards and by using THF as eluant at a flow rate of 0.5 mL/min.

Electron spectroscopy for chemical analysis (ESCA) was performed on the PACS powder by using a monochromatic AlK_{α} radiation 5950 Hewlett-Packard photoelectron spectrometer with a resolution at 0.8 eV. Samples were Ar^{+} ion etched to ensure clean surfaces prior to analysis. Spectra were determined at room temperature with a pressure under 10^{-7} Torr.

Al content in the PACS was determined by Central South Institute of Mining and Metallurgy of China by using a chemical method, and the oxygen content of PACS and PCS were analyzed instrumentally in the National Key Lab of Powder Metallurgy in China.

RESULTS AND DISCUSSION

To study the reaction mechanism between PCS and $Al(AcAc)_3$, the pale yellow byproducts were characterized by GC/MS to determine its components. Figure 1 shows the gas chromatogram of the byproduct. Five peaks were detected and the corresponding compounds were analyzed by MS as shown in Figure 2. Based on the MS spectra and the matched GC retention times, the five main peaks were assigned to 3-methoxy-2,2-dimethyl-oxirane, 2,3-dihydro-[1,4]dioxine, pent-3-en-2-one, acetylacetone, and 3-ethyl-but-3-en-2-one, respectively. According to the byproducts, at least three kinds of reaction had presumably occurred when PCS was heated with $Al(AcAc)_3$ in nitrogen, as shown in Scheme 1. Acetylacetone is presumably formed by the reaction as described by Scheme 1(a). In this reaction, the latent reactive Si—H of PCS transfers its H to the 3-C of the chelating acetylacetone in $Al(AcAc)_3$, resulting in the evolution of acetylacetone and the formation of Si—Al—Si bonds at 310°C. This experimental data support the reaction mechanism initially reported by Ishikawa et al.⁴

In addition to acetylacetone, the formation of pent-3-en-2-one as another byproduct can be explained by Scheme 1(b). The Si—H hydrogen of PCS is transferred to the 2-C of the chelating acetylacetone of $Al(AcAc)_3$, which readily causes the cleavage of the C—O on $Al(AcAc)_3$, producing the byproduct and an Al—O—Si moiety on the PCS chain. The formation of 2,3-dihydro-[1,4]dioxine in the reaction between PCS and $Al(AcAc)_3$

can be interpreted as shown by Scheme 1(c). At 310°C, in the presence of PCS, the acetylacetone chelating group of $Al(AcAc)_3$ is presumably decomposed into radicals and then rearranged as 2,3-dihydro-[1,4]dioxine. As shown in Scheme 1(a,b), PCS might activate the decomposition of $Al(AcAc)_3$ at relatively low temperature. The interpretation of the resulting 3-ethyl-but-3-en-2-one, 3-methoxy-2,2-dimethyl-oxirane in the synthesis of PACS needs further investigation.

Figure 3 shows the IR spectra of PACS and the PCS feed stock. Contrasting with PCS, additional peaks were observed at 1594 cm^{-1} (C=O stretching) and 1531 cm^{-1} (C=C stretching) in the IR spectrum of PACS, which were attributed to the residual groups of the $Al(AcAc)_3$ reacting with the PCS.² The IR absorption intensity ratio of Si—H/

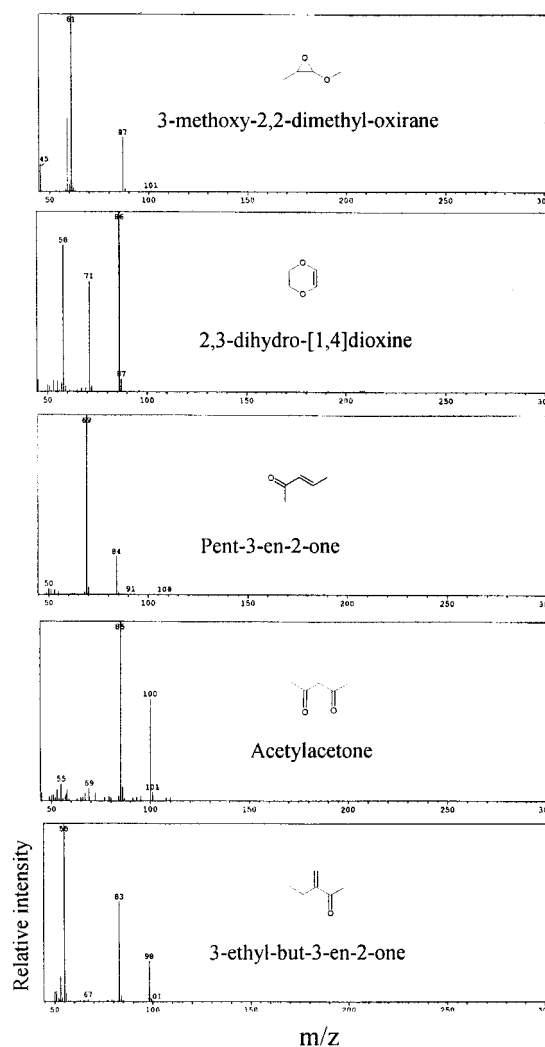
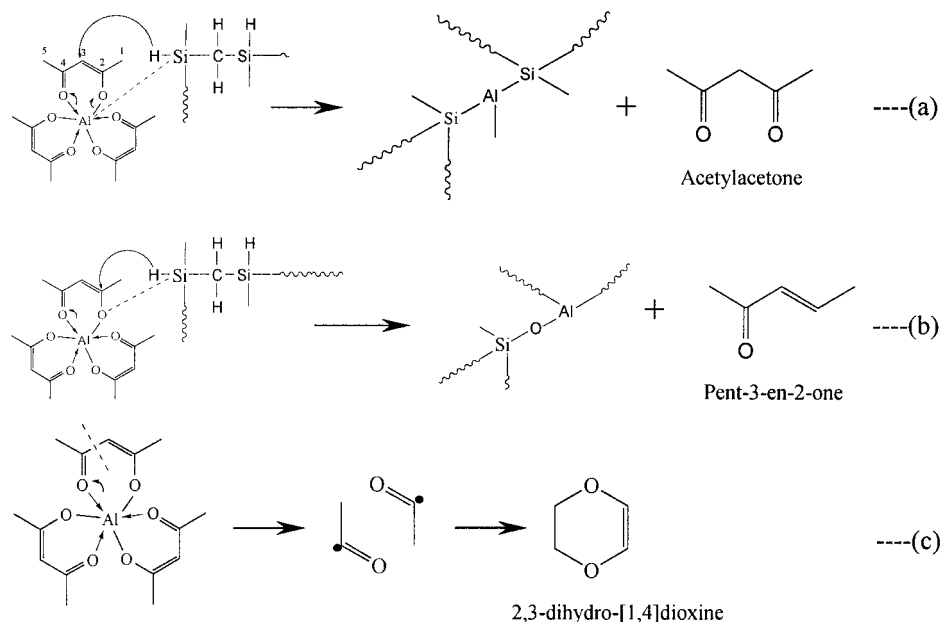


Figure 2 Mass spectra corresponding to the main peaks of gas chromatograms.



Scheme 1 The mechanisms of the reaction between PCS and $\text{Al}(\text{AcAc})_3$.

$\text{Si}-\text{Me}$ (2100 and 1250 cm^{-1} , respectively) changed from 0.73 to 0.5 , whereas that of PCS without $\text{Al}(\text{AcAc})_3$ at 310°C in N_2 showed no such ratio change, because the PCS is stable at 310°C in the inert atmosphere.¹ This proved that $\text{Si}-\text{H}$ in PCS was consumed to produce dehydrogenative crosslinked $\text{Si}-\text{Al}$ bonds as well as the reactions of Scheme 1(a,b). Ishikawa² reported similar results on polyzirconocarbosilane synthesized by reaction between PCS and zirconium acetylacetonate. However, the corresponding peaks of $\text{Si}-\text{Al}-\text{Si}$ and $\text{Si}-\text{O}-\text{Al}$ bonds were not observed in the IR spectra, which may be attributed

to the fact that the weak absorption peaks of $\text{Al}-\text{Si}$ and $\text{O}-\text{Al}$ overlapped with the broad $\text{Si}-\text{O}$ ($1005\text{--}1112\text{ cm}^{-1}$)⁵ and $\text{Si}-\text{C}$ ($1122, 790, 486\text{ cm}^{-1}$)⁶ absorption peaks. Although no reports about the overlapped IR absorption peaks of $\text{Si}-\text{Al}$ with $\text{Si}-\text{O}$ or $\text{Si}-\text{C}$ have been made, this remains likely because all the peaks ($\text{Si}-\text{Al}$, $\text{Si}-\text{O}$, $\text{Al}-\text{O}$, and $\text{Si}-\text{C}$) should present at low wave numbers. The concentration of $\text{Al}-\text{Si}$ is also much lower than that of $\text{Si}-\text{O}$, $\text{Al}-\text{O}$, and $\text{Si}-\text{C}$, and this is another reason for the absence of the $\text{Si}-\text{Al}$ IR peaks in Figure 3.

Figure 4 shows the molecular weight distribu-

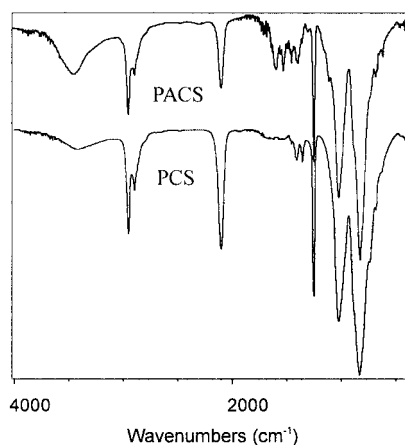


Figure 3 IR spectrum of PACS and PCS feed stock [weight ratio: $\text{Al}(\text{AcAc})_3/\text{PCS} = 1/2.33$].

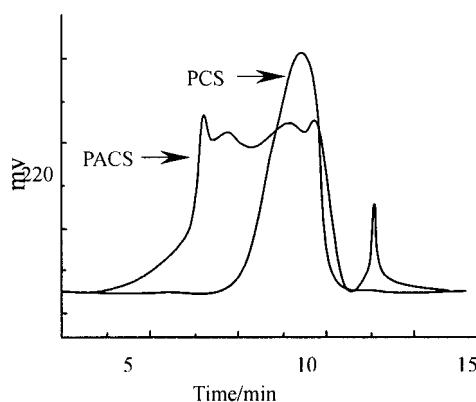


Figure 4 Molecular weight distribution of PACS and PCS feed stock [with weight ratio: $\text{Al}(\text{AcAc})_3/\text{PCS} = 1/2.33$].

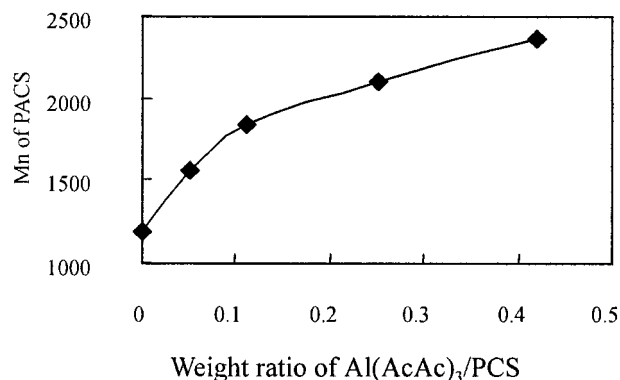


Figure 5 M_n of PACS as function of weight ratio of Al(AcAc)₃/PCS.

tion of PACS and the PCS feed stock. It is evident that the molecular weight of the PACS became significantly higher than that of the PCS feed stock. This indicates that the PCS molecules were crosslinked by reaction with Al(AcAc)₃, which subsequently formed Si—Al—Si and Si—O—Al bonds as described above. Figure 5 shows the molecular weight of PACS as a function of the reaction ratio of Al(AcAc)₃/PCS. Generally, the molecular weight of PACS increases at higher Al(AcAc)₃/PCS ratios. When the ratio of Al(AcAc)₃/PCS was 1/2.33, the number average molecular weight of the PACS reached about 2400, twice that of the PCS feed stock.

The ESCA spectrum of PACS is shown in Figure 6. In addition to the peaks (Si, C, O) assigned to PCS,⁷ PACS displayed an additional Al_{2p} peak at 72–78 eV, evidencing the presence of Al.⁸ Furthermore, the peak ratio of O_{1s}/C_{1s} of PACS was higher than that of the PCS feed stock,⁹ which

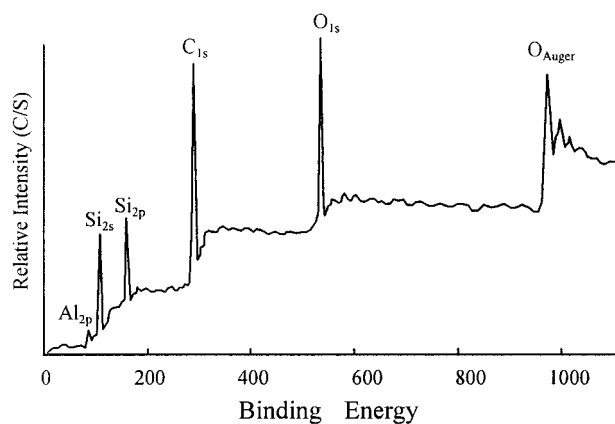


Figure 6 ESCA spectrum of PACS [with weight ratio: Al(AcAc)₃/PCS = 1/2.33].

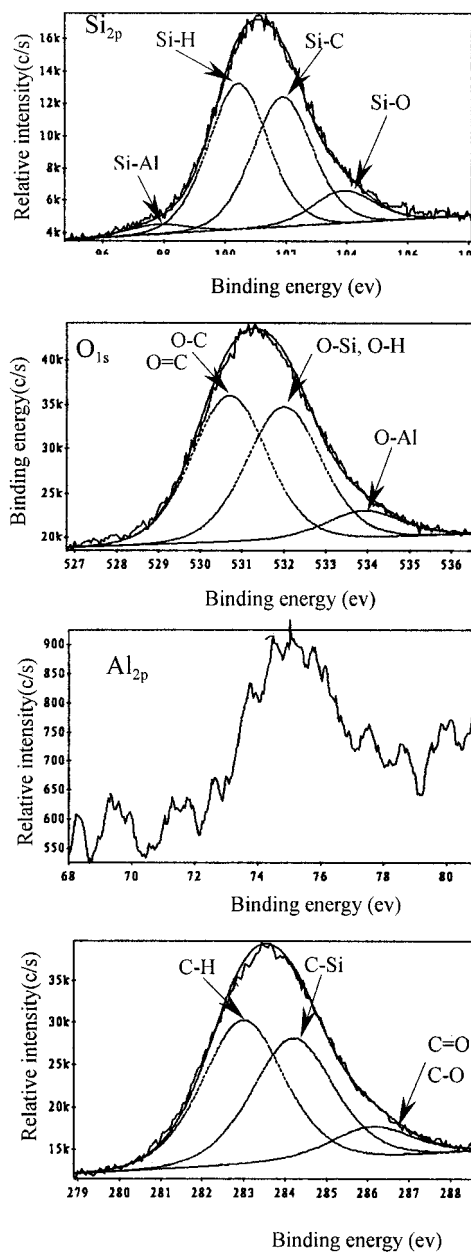


Figure 7 Deconvolution of the ESCA Si_{2p}, O_{1s}, Al_{2p}, and C_{1s} of PACS [with weight ratio: Al(AcAc)₃/PCS = 1/2.33, corresponding weight ratio of Al/PCS = 3.6/100].

indicated the higher oxygen content of PACS. The deconvolution of ESCA Si_{2p}, O_{1s}, C_{1s}, and Al_{2p} peaks is shown in Figure 7. ESCA Al_{2p} was present at low intensity, presumably due to low content of Al. The Si_{2p} peak was deconvoluted into 104.2, 102.1, and 100.5 eV and assigned to bonds of Si—O, Si—C, and Si—H,^{5,6,10} respectively. Based on the integration of each peak, Si

Table I Elemental Analysis of PACS and PCS Feed Stock

Ratio (wt %) of Al(AcAc) ₃ /PCS	Al Content of PACS (wt %)	O content of PACS (wt %)
1/19	0.37	—
1/9	0.63	2.14
1/4	1.87	—
1/2.33	2.31	4.21
PCS feed stock	0	1.34

was bonded to mainly C, H, and weakly to O. It is noteworthy that the weak peak at 98 eV was probably due to the Si—Al bond, as described in Scheme 1(a). This binding energy is lower than that of Si—C and Si—O, which is in agreement with the weaker nature of the Si—Al bond than Si—C or Si—O. The deconvoluted peaks of ESCA O_{1s} centered at 534.3 and 530.9 eV were assigned to O—Al and O—C, respectively.¹¹ The peak centered at 532.4 eV was assigned to O—Si and O—H,¹¹ because their binding energies are close. The deconvoluted ESCA of C_{1s} incorporated C—H (283.0 eV), C—Si (284.5 eV), and C—O C=O (286.4 eV)^{11,12}; the binding energies of C—O and C=O were also near.¹³

Table I presents elemental analysis of the PACS and PCS feed stock demonstrates that Al was incorporated into PACS together with oxygen, which corresponded to the ESCA data. As the mixing ratio of Al(AcAc)₃/PCS increased, additional oxygen was introduced into PACS with the increased Al content.

CONCLUSION

Polyaluminocarbosilane (PACS), a precursor of highly temperature-resistant SiC fibers, was synthesized by reaction between PCS and Al(AcAc)₃ at 310°C under ambient pressure. The reaction mechanism was studied by analyzing the structure of PACS and the condensed byproducts. In addition to the formation of Si—Al—Si bonds, which has been reported previously, novel Si—

O—Al bonds were identified as a result of the reaction. On the other hand, we also detected as byproducts 3-methoxy-2,2-dimethyl-oxirane, 2,3-dihydro-[1,4]dioxine, pent-3-en-2-one, and 3-ethyl-but-3-en-2-one besides acetylacetone, as reported previously. The mechanism of the reaction between PCS and Al(AcAc)₃ is more complex than indicated previously.

This work was supported by the Chinese Natural Science Fund under Grant 59972042 and the Korea Science and Engineering Foundation (KoSEF) Grant 2000-2-30700-007-3.

REFERENCES

1. Birot, M.; Pillot, J. P.; Dunoguès, J. *Chem Rev* 1995, 95, 1443.
2. Ishikawa, T.; Kohtoku, Y.; Kumagawa, K. *J Mater Sci* 1998, 33, 161.
3. Soraru, G. D.; Mercadini, M.; Maschio, R. D. *J Am Ceram Soc* 1993, 76, 2595.
4. Ishikawa, T.; Kohtoku, Y.; Kumagawa, K.; Yamamura, T.; Nagasawa, T. *Nature* 1998, 391, 19.
5. Ikeda, A.; Sadou, T.; Nagashima, H.; Kouno, K.; Yoshikawa, N.; Tshukamoto, K.; Kuroki, Y. *Thin Solid Films* 1999, 345, 172.
6. Padhi, B. K.; Patnail, C. *Ceram Int* 1995, 21, 213.
7. Bouillon, E.; Langlais, F.; Pailler, R.; Naslain, R.; Cruege, F.; Huong, P. V.; Sarthou, J. C.; Deppuech, A.; Laffon, C.; Lagarde, P.; Monthieux, M. *J Mater Sci* 1991, 26, 1333.
8. Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.; Physical Electronics Division, 1979.
9. Li, X. X. Ph.D. thesis; The Study of the Processes for Polycarbosilane-Derived SiC Fibers; National University of Defense Technology, Changsha, P.R. China, 1998.
10. Vincent, C.; Vincent, H.; Berthet, M. P.; Piquero, T.; Bouix, J. *Compos Part A—Appl S* 1996, 27 (5), 365.
11. Hirahama, M. K. N.; Caseri, W. R.; Suter, U. W. *Appl Surf Sci* 1999, 143, 256.
12. Desimoni, E.; Casella, G. I.; Salvi, A. M.; Cataldi, T. R. I.; Morone, A. *Carbon* 1994, 30 (4), 527.
13. Yung, K. C.; Zeng, D. W.; Yue, T. M. *Appl Surf Sci* 2001, 173, 193.