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Curing and pyrolysis of polysiloxane/divinylbenzene and its derived carbon fiber reinforced Si—O—C composites

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The curing and pyrolysis of hydrogen-containing polysiloxane (PSO) and divinylbenzene (DVB) were investigated in this paper. It was found that H_2PtCl_6 was an effective catalyst for the curing of DVB/PSO. The mass ratio of DVB/PSO had great effect on ceramic yield. The cured DVB/PSO with a mass ratio of 0.5:1 had the highest ceramic yield (76%) at temperature up to 1000°C, and its pyrolysates consisted of 38.3 wt% silicon, 27.4 wt% oxygen, and 34.3 wt% carbon of which 26.3 wt% was free carbon. The composition and structure of pyrolysates of DVB/PSO were changed with increasing pyrolysis temperature. The pyrolysis behavior of DVB/PSO was characterized by thermal analysis. DVB/PSO-derived Si—O—C composites reinforced with carbon fiber cloth (C_f/Si—O—C) were fabricated. The results showed that the flexural strength of C_f/Si—O—C composites could be increased from 118.00 ± 5.00 MPa to 139.78 ± 7.68 MPa if the pyrolysis temperature was elevated from 1000 to 1400°C, which was ascribed to the weakened interfacial bonding.

1. Introduction

The preceramic polymer pyrolysis route to processing of ceramics and ceramic matrix composites (CMCs) is being actively developed because it offers many potential advantages such as low processing temperature, controllable ceramic compositions, and near-net-shape technologies. Many different preceramic polymers have been discovered since their original development by Yajima *et al.* [1]. Of all the preceramic polymers, polysiloxane (PSO) has attracted increasing interest in recent years [2]. It is not only commercially available but also very cheap, and its derived silicon oxycarbide (Si—O—C) (in Ar or N_2) and silicon oxynitride (Si—N—O) (in NH_3) ceramics have been demonstrated to possess improved properties such as creep resistance and microstructural stability over those of many conventional silicate ceramics [3, 4]. Therefore, PSO is considered as a desirable precursor for low-cost ceramics and CMCs with high performance.

The manufacturing of ceramics and CMCs via preceramic polymer pyrolysis includes three stages. In stage 1, preceramic polymers are made into complex shapes in various forms such as fibres, coatings, and bulk bodies by conventional polymer processing techniques. In stage 2, the preceramic polymers are cured into solids to render the article infusible and insoluble and retaining its form, and also subsequently enabling a higher ceramic yield. In stage 3, the cured solids are pyrolyzed in inert or reactive environment to obtain ceramics.

In the present work, a hydrogen-containing PSO was used as precursor to Si—O—C ceramics, and divinylbenzene (DVB) as cross-linking reagent for PSO. The cure and pyrolysis behaviors of PSO/DVB were investigated firstly. PSO/DVB derived Si—O—C composites reinforced with carbon fiber cloth were fabricated subsequently, and their microstructure and properties were characterized.

2. Experimental procedure

2.1. Cure and pyrolysis of PSO/DVB

PSO, a colorless transparent liquid containing 1.4 wt% hydrogen, was selected as the precursor to Si—O—C ceramics. DVB, a light yellow transparent liquid, was selected as the cross-linking reagent for PSO. Chloroplatinic acid (H_2PtCl_6), dissolved in anhydrous ethanol, was used as the catalyst.

PSO and DVB were mixed and stirred powerfully. During stirring, H_2PtCl_6/ethanol solution was dropped into PSO/DVB solution. After being stirred for a period of time, the PSO/DVB solution was cured at preset temperatures for 6 h under the protection of high purity N_2(99.999%). The cured PSO/DVB were then pyrolyzed at different temperatures with high purity flowing N_2 as a protective atmosphere.

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The types of chemical bonds of cured PSO/DVB and its pyrolysates were characterized by FTIR. The chemical analysis was performed on the pyrolysates. The C analysis was performed using combustion techniques. The Si analysis was performed using Atomic Absorption Spectroscopy after digestion of the pyrolysates. Oxygen analysis was not performed. Thermal decomposition of the cured PSO/DVB up to 1200°C in N_2 was investigated by simultaneous thermal gravimetric analysis (TG), differential thermal gravimetric analysis (DTG) and differential thermal analysis (DTA) carried out with a NETZSCH STA 449C Thermal System at heating rates of 5, 10, 15, 20, 25, 30°C/min, respectively. A high purity nitrogen flow 20 $cm^3\ min^{-1}$ was used prior to and during pyrolysis.

2.2. Fabrication and characterization of C_f/Si–O–C composites

Plain weave cloths of carbon fibers were used as reinforcement. The tensile strength and elastic modulus of carbon fibers were 3500 MPa and 210 GPa, respectively.

Twelve layers of carbon fiber cloths were stacked into a laminate panel with the sequence of 0°/0°. Then, the panel was placed into a mold. The mold was first evacuated, followed by the introduction of PSO/DVB solution into mold. Following the vacuum infiltration, the mold was heated at 120°C for 6 h. After curing, the cured panel was taken out from mold and pyrolyzed at 1100°C for 30 min with a heating rate of 10°C/min. High purity flowing N_2 was used as the protective atmosphere. Then, the panel was further densified by repeating fourteen cycles of vacuum infiltration and pyrolysis under the same conditions until the weight gain of the panel was less than 1 wt%. The resulting sample was denoted as T-1000. Another sample denoted as T-1400 was fabricated under the same processing conditions as sample T-1000 except that the 14th pyrolysis was performed at 1400°C for 30 min with a heating rate of 30°/min.

The bulk density of C_f/Si–O–C composites was measured according to Archimede's principle with deionized water as the immersion medium. The flexural strength was tested by a three-point bending method with the span/height ratio of 15 and a cross-head speed of 0.5 mm/min. For flexure testing, five specimens were measured. After the tests, scanning electron microscopy (SEM) was employed to observe the fracture surfaces of the composites.

3. Results and discussion

3.1. Gel content and ceramic yield of PSO/DVB

Using the preceramic polymer pyrolysis processing route, high ceramic yield is desirable because the stress resulting from volume shrinkage during pyrolysis will be reduced if the preceramic polymer has a high ceramic yield. In order to obtain a high ceramic yield, a high degree of curing is necessary. The effects of catalyst content, mass ratio of DVB/PSO and curing temperature on the degree of curing and ceramic yield were investigated in this paper.

TABLE I The effects of catalyst content on gel content and ceramic yield of DVB/PSO

Catalyst content (ppm)	Gel content (%)	Ceramic yield (%)	Relative absorbency of Si–H
0	23.5	32.7	0.863
3.77	98.1	66.8	0.680
7.54	98.6	66.1	0.560
11.31	98.7	65.6	0.546

Mass ratio of PSO/DVB was 1:1, and curing temperature was 120°C. Relative absorbency of Si–H was referred to as the ratio of height of Si–H absorption peak (2160 cm^{-1}) to that of Si–CH_3 absorption peak (1260 cm^{-1}). The relative absorbency of Si–H of DVB/PSO before curing was 1.226.

Table I shows the effects of catalyst content (mass ratio of Pt element in H_2PtCl_6 to PSO + DVB) on gel content (wt. of dried residues after cured DVB/PSO was immersed in flowing benzene for 24 h/wt. of cured DVB/PSO) and ceramic yield (wt. of products pyrolyzed at 1000° with a heating rate of 1°C/min/wt. of cured DVB/PSO).

As shown in Table I, the gel content of PSO/DVB cured without catalyst is only 23.5%, suggesting that the product contained many uncured precursor molecules. These uncured precursor molecules were evolved during pyrolysis, resulting in the low ceramic yield (only 32.7%). When catalyzed with H_2PtCl_6, the gel content and ceramic yield were increased markedly to about 98 and 66%, respectively, demonstrating that H_2PtCl_6 is an effective catalyst for the curing of DVB/PSO. The high gel content and ceramic yield implied that most precursor molecules were cured into a solid network. The hydrosilylation reaction between Si–H in PSO and C=C in DVB was responsible for the curing of DVB/PSO. The relative absorbency of Si–H (denoted as $A_{Si–H}$) of DVB/PSO before curing was 1.226. The $A_{Si–H}$ decreased to 0.863 after curing at 120°C without a catalyst, suggesting that 29.6% of Si–H bonds took part in the hydrosilylation reaction. The $A_{Si–H}$ decreased gradually with the increase of catalyst content, suggesting that there were increasing numbers of Si–H bonds participating in the hydrosilylation reaction. Accordingly, the number of uncured precursor molecules was reduced and the gel content and ceramic yield of DVB/PSO increased gradually.

The effects of mass ratio of DVB/PSO on gel content and ceramic yield are presented in Table II. Table II shows that the cured samples had low gel content when the mass ratio of DVB/PSO was less than 0.3:1. Consequently, their ceramic yields were low for the reason stated in the previous paragraph. When DVB/PSO $\geq$ 0.3:1, the cured samples had almost equal gel contents, but their ceramic yields were different. The decrease of ceramic yield with increasing mass ratio of DVB/PSO was due to the low ceramic yield of DVB (16.3%). The cured DVB/PSO with a mass ratio of 0.5:1 had the highest ceramic yield (76%). The DVB/PSO solution with a mass ratio of 0.5:1 was selected to fabricate composites.

The gel content and ceramic yield of DVB/PSO cured at different temperatures are shown in Table III. It is

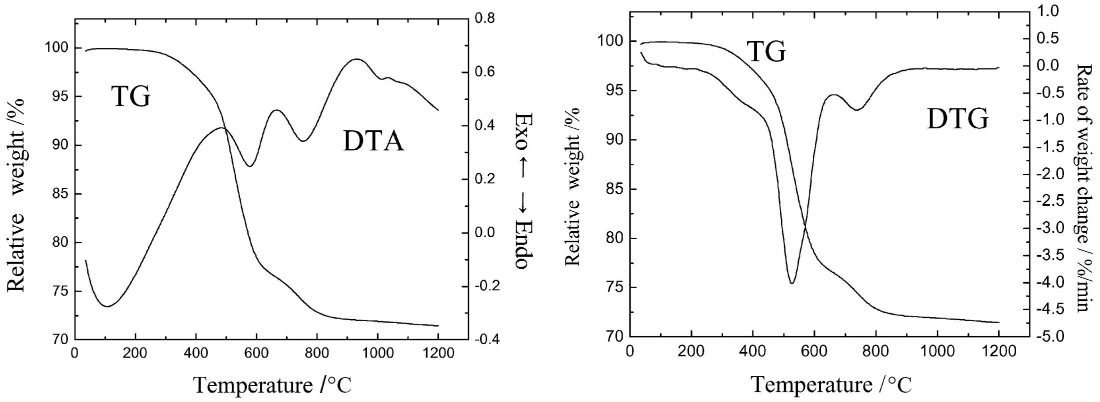


Figure 1 TG/DTG/DTA analysis of cured DVB/HPSO when heated from room temperature to 1200°C under flowing N_2.

TABLE II The effects of mass ratio of DVB/PSO on gel content and ceramic yield

Mass ratio of DVB/PSO	Gel content (%)	Ceramic yield (%)
0.05:1	62.5	47.1
0.1:1	70.5	47.7
0.3:1	98.3	72.0
0.5:1	99.3	76.0
0.7:1	99.0	72.1
1.0:1	98.7	65.6
1.4:1	99.0	57.2
1.7:1	98.2	51.7

Catalyst content was 11.31 ppm, and curing temperature was 120°C.

TABLE III Gel content and ceramic yield of DVB/PSO cured at different temperatures

Curing temperature (°C)	Gel content (%)	Ceramic yield (%)
60	96.5	72.5
80	98.2	73.9
100	99.2	74.4
120	99.3	76.0
150	99.7	75.4
180	99.4	74.5

Catalyst content was 11.31 ppm, and mass ratio of DVB/PSO was 0.5:1.

evident that varying the curing temperatures from 60 to 180°C did not change the gel content and ceramic yield much, indicating that the curing temperature did not have significant effects on the gel content and ceramic yield of DVB/PSO.

3.2. Pyrolysis behavior of cured PSO/DVB

The pyrolysis behavior of the cured DVB/PSO with a mass ratio of 0.5:1 was characterized by TG, DTG and DTA with a heating rate of 25°C/min. The result is shown in Fig. 1. It is clear from Fig. 1 that the pyrolysis weight loss began at approximately 370°C and was completed by 800°C. In this temperature range, dissociation reactions involving the cleavage of chemical bonds such as Si—C, Si—H, C—C and C—H and thermal redistribution reactions involving the exchange of Si—O, Si—H and Si—C occurred and gases such as methane, ethylene, hydrogen and C_3 and C_4 hydrocarbons were generated [5–8]. It can be seen from Fig. 1 that the DTG curve showed two peaks centered at 525 and 740°C, indicating two pyrolysis steps. Accordingly, the DTA curve showed two endothermic peaks centered at 580 and 750°C. Activation energies of the two pyrolysis steps, which were obtained from TG and DTG analysis under different heating schedules, are shown in Table IV. The activation energies (208.4 and 339.9 kJ/mol), which lead to the cleavage of Si—C, Si—H and C—H, were in reasonable agreement with the values of 263 and 387 kJ/mol that were reported for thermal degradation of polysiloxane resin [9].

TABLE IV Activation energies of the two pyrolysis steps of cured DVB/PSO

Pyrolysis step	Temperature regime	Activation energy (kJ/mol)
1st	420–610°C	208.4
2nd	620–800°C	339.9

3.3. Characterization of the pyrolysates of PSO/DVB

Fig. 2 shows FTIR spectra of the pyrolysates of DVB/PSO pyrolyzed at different temperatures. Besides

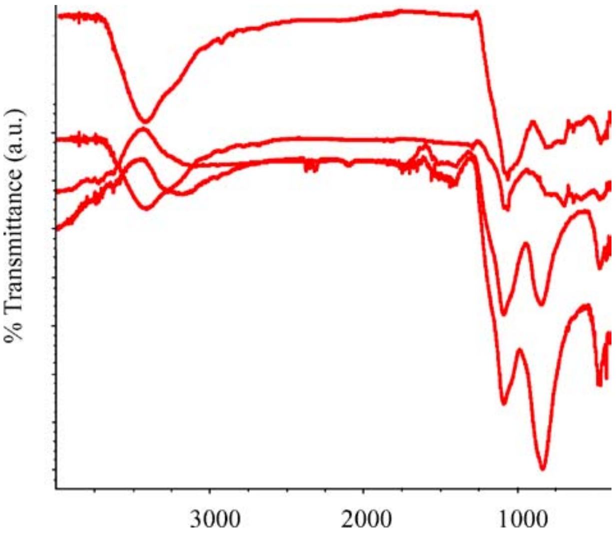
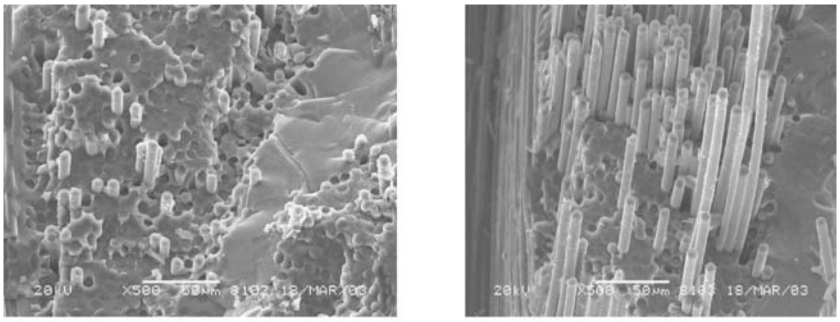


Figure 2 FTIR spectra of pyrolysates of DVB/PSO at different temperatures.



(a) (b)

Figure 3 Fracture surfaces of sample T-1000 (a) and sample T-1400 (b).

the absorption peak at 3400 cm^{-1} attributed to adsorbed H_2O, there were three absorption peaks at 1060, 800, and 460 cm^{-1} in the spectra of the products pyrolyzed at 1000 and 1200°C, respectively. There was no absorption peak corresponding to hydrogen-containing radicals in the spectrum of the product pyrolyzed at 1000°C, indicating that there was little hydrogen in the pyrolysates. In the spectra of the products pyrolyzed at 1400 and 1600°C, there were three absorption peaks at 1090, 830 and 460 cm^{-1}, respectively.

The peaks at 800 and 460 cm^{-1} in the spectra of the products pyrolyzed at 1000 and 1200°C were attributed to O—Si—O band bending and Si—O—Si band rocking vibrational modes, respectively [10]. The shift of the peak at 1090 cm^{-1}, due to stretching vibration of Si—O, to 1060 cm^{-1} was caused by the smaller electronegativity of a carbon substituent compared with an oxygen atom [11]. That there is only a peak at 1060 cm^{-1} and not two separate peaks at 1090 and 830 cm^{-1} due to the Si—C band stretching vibrational mode indicated that the silicon oxycarbide structure was not a mixture of [SiO_4] and [SiC_4]. The structure is a three-dimensional random network of silicon-oxygen tetrahedral with some silicons bonded to one or two carbons substituted for oxygen which were in turn tetrahedrally bonded to other silicon atoms, because no carbon-oxygen bonds were observed in pyrolysates of polysiloxane, as determined by FTIR and XPS [3]. When pyrolysis temperatures were elevated to 1400°C or above, the peak at 1060 cm^{-1} disappeared and the peaks at 1090 and 830 cm^{-1} appeared, indicating that the random network had transformed to [SiO_4] and [SiC_4] as a result of a carbothermal reduction into SiO_2, SiC, SiO and CO [12].

Based on the results of FTIR, it can be demonstrated that polysiloxane-derived silicon oxycarbide could be stable to as high as 1200°C.

Table V shows the compositions of the pyrolysates of DVB/PSO pyrolyzed at different temperatures. The products of DVB/PSO pyrolyzed at 1000°C consisted of 38.3 wt% silicon, 27.4 wt% oxygen and 34.3 wt% carbon of which 26.3 wt% was free carbon determined by chemical analysis. The oxygen content was determined on the premise that the pyrolysates contained only silicon, oxygen and carbon, which had been shown in another study [2]. The contents of Si, C, and O were changed with increasing pyrolysis temperature, which was also a result of the carbothermal reduction reaction.

TABLE V Compositions of pyrolysates of DVB/PSO pyrolyzed at different temperatures

Temperature (°C)	Si (wt%)	C (wt%)	O (wt%)	Empirical formula
1000	38.33	34.34	27.33	$SiO_{1.25}C_{2.09}$
1200	38.33	38.30	23.37	$SiO_{1.07}C_{2.33}$
1400	38.61	38.52	22.87	$SiO_{1.04}C_{2.33}$
1600	40.43	37.35	22.22	$SiO_{0.96}C_{2.16}$

3.4. Flexural strength and microstructure of C_f/Si—O—C composites

The density and flexural strength of sample T-1000 were 1785 kg/m^3 and 118.00 ± 5.00 MPa, respectively, and the flexural strength of sample T-1400 was 139.78 ± 7.68 MPa. Fig. 3 shows fracture surfaces of sample T-1000 and T-1400. It can be seen that sample T-1000 (Fig. 3a) illustrated flat fracture surface with very short fibre pull-out, indicating that fiber-matrix bonding was very strong. In this sample, it was found that Si atoms diffused into carbon fibers during fabrication, as shown in Fig. 4. It has been documented that the atoms in the matrix can diffuse into or react with carbon fibers during pyrolysis to create strong fiber-matrix bonding and a great reduction in fiber strength [13, 14]. Consequently, sample T-1000 exhibited typical brittle fracture behavior (Fig. 5a) and low flexural strength.

In the SEM photo of fracture surface of sample T-1400 (Fig. 3b), many pulled-out fibers were observed, and the pull-out length was much longer than that of sample T-1000, indicating that fiber-matrix bonding was weaker than that of sample T-1000. The weaker interfacial bonding of sample T-1400 may be attributed

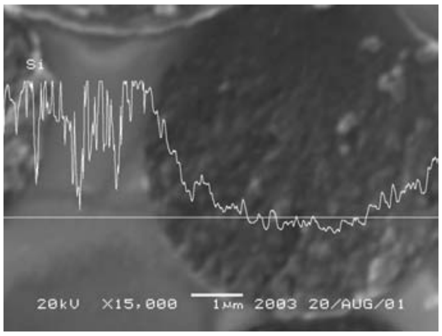
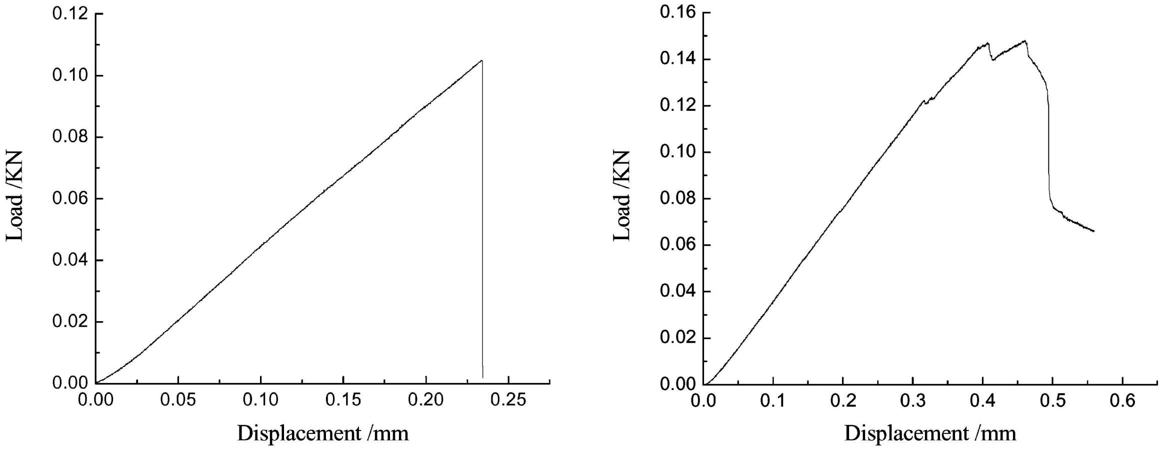


Figure 4 Characteristic X-ray line profile of Si in sample T-1000.



(a) (b)

Figure 5 Load-displacement curves of sample T-1000 (a) and T-1400 (b).

to decomposition at the fiber-matrix interface resulting from the diffusion of Si atoms into carbon fibers. Although how Si atoms diffuse into carbon fibers is not clear so far, it is proposed that the interface consisted of Si, C, and O in which oxygen atoms were derived from the surface sizing of carbon fibers or the Si—O—C matrix. According to the results of FTIR, the interface would decompose at 1400°C. As a result of the decomposition of the interface, fiber-matrix bonding became weak and *in-situ* strength of carbon fibers increased. Therefore, sample T-1400 exhibited tough fracture behavior (Fig. 5b) and higher flexural strength than that of sample T-1000.

4. Conclusions

When catalyzed with H_2PtCl_6, PSO and DVB cure into hard solids with high ceramic yield after pyrolysis. The curing temperature did not significantly change the degree of curing or the ceramic yield of DVB/PSO. However, the mass ratio of DVB/PSO had significant effect on ceramic yield. The cured DVB/PSO with a mass ratio of 0.5:1 had the highest ceramic yield (76%) at temperatures up to 1000°C, and its pyrolysates consisted of 38.3 wt% silicon, 27.4 wt% oxygen and 34.3 wt% carbon of which 26.3 wt% was free carbon. The composition and structure of pyrolysates of DVB/PSO changed with increasing pyrolysis temperature. Pyrolysis weight loss of DVB/PSO mainly occurred during 370–800°C in which the pyrolysis of DVB/PSO included two steps.

DVB/PSO solution with a mass ratio of 0.5:1 was used to fabricate C_f/Si—O—C composites. It was found that the flexural strength of C_f/Si—O—C composites was increased from 118.00 ± 5.00 MPa to 139.78 ± 7.68 MPa when the pyrolysis temperature was elevated from 1000 to 1400°C, which was ascribed to the weakened interfacial bonding between the carbon fibers and the matrix.

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