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Synthesis of a minute SiC product from polyvinylsilane with radiation curing: Part II—Ceramization process of radiation cured polyvinylsilane

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Abstract We have synthesized minute SiC products from polyvinylsilane (PVS), which is a liquid organosilicon polymer, with radiation curing. Since there is a close relationship between the properties of obtained SiC products and pyrolysis condition, it is important to investigate the ceramization process of cured PVS in order to find out the optimum pyrolysis condition. In this paper, the ceramization process of the PVS cured by γ-ray irradiation at room temperature was investigated by gas analysis, thermogravimetric analysis (TGA), density measurement, and so on. It was found that the ceramization of γ-ray cured PVS starts above 500 K, and drastic organic–inorganic conversion occurs in the temperature range of 700–1100 K. According to the changes of mass and density, it was found that the volume shrinkage of PVS during the curing and pyrolysis processes is 80%. The SiC obtained by pyrolysis at 1573 K in argon gas atmosphere showed the density of 2500 kg/m^3 and microvickers hardness of 31.6 GPa.

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Introduction

Ceramic materials, which have excellent properties of heat resistance, chemical stability, piezoelectricity, and so on, are expected to be applied for microelectromechanical systems (MEMS) available in severe environment such as high temperature, and/or corrosive environment. By using the MEMS technology, it is expected that a maintenance system which works in hazardous environment in place of human being, and a medical appliance for the treatment in a blood vessel will be realized. So far, several researchers have reported about fabrication of minute ceramic products of Si–C, Si–C–N, and so on [1–6].

In order to fabricate such minute ceramic products, the pyrolysis of preceramic polymer is a most advantageous method, because the preceramic polymers have high formability. We have examined synthesis of a minute SiC product with the size ranging from several μm to several mm from preceramic polymer with radiation curing by following process: (1) injection of preceramic polymer into a mold, (2) radiation curing of the polymer, and (3) pyrolysis of the cured polymer in an inert gas atmosphere. We have selected polyvinylsilane (PVS), which is a liquid organosilicon polymer at room temperature, as a starting material, and reported about the irradiation effect on the PVS and the optimum curing condition [7]. In recently, we have succeeded in fabricating a minute SiC product with a gear shape, as shown in Fig. 1.

By the way, it is necessary to find out the optimum pyrolysis condition of the cured PVS in order to fabricate minute SiC products with high performance, because there is a close relationship between the properties of obtained SiC and the

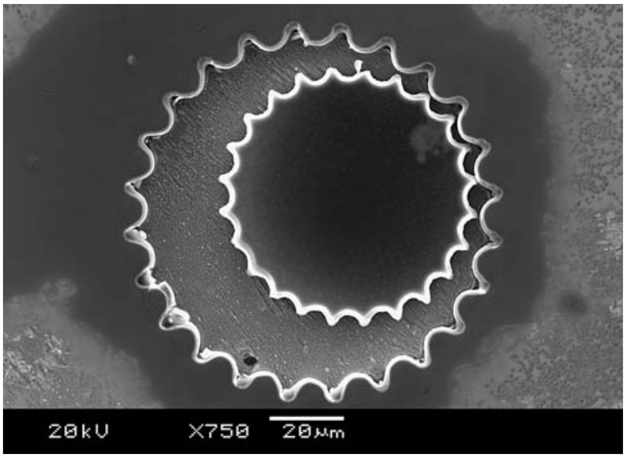

Fig. 1 A minute SiC product with a gear shape synthesized from PVS with radiation curing

pyrolysis condition. In this paper, the ceramization process of γ-ray cured PVS was investigated, and the optimum condition for the pyrolysis of cured PVS was discussed. Furthermore, on the view point of size accuracy, it is important to estimate the volume shrinkage of PVS in pyrolysis process. We examined a method to estimate the volume shrinkage from the changes of mass and density of PVS during the pyrolysis process.

Experimental procedure

Material and γ-ray irradiation

Polyvinylsilane (PVS) is synthesized by radical polymerization of vinylsilane ($CH_2{=}CHSiH_3$) in an autocrave using azobis(isobutyronitrile) (AIBN) [8]. The vinylsilane of about 130 mmol and the AIBN of about 2.5 mmol were reacted in toluene at 353 K for 8 h under a nitrogen atmosphere. The chemical structure of PVS determined from NMR data is represented as $[-CH_2CH_2SiH_2-]_n[-CH_2CH(SiH_3)-]_{n'}$, and the unit ratio of n/n' is almost 1. The PVS is a viscous liquid polymer with viscosity of about 200 mPa s at 298 K, and has a weight average molecular weight (M_w) of 2.8×10^3, a number average molecular weight (M_n) of 9.6×10^2, and a molecular weight distribution (M_w/M_n) of 2.90 (polystyrene equivalent).

The PVS was put into a glass tube, and then the tube was evacuated and sealed. The PVS was irradiated by ^{60}Co γ-ray at dose rate of 30 kGy/h and with dose of 3 MGy at room temperature under vacuum. The dose of 3 MGy is a sufficient dose for the PVS to be crosslinked and solidified [7].

Measurements and analyses

The gases evolved from the irradiated PVS during heat treatment were measured as following. A quartz tube containing the irradiated PVS was evacuated, heated up to 473 K with the heating rate of 300 K/h, held for 30 min at 473 K, and cooled by furnace cooling. The gases accumulated in the tube were measured by gas chromatograph (Gas Chromatograph 163, Hitachi). After the measurement of evolved gases, the tube was evacuated again, and heated up to 100 K higher (573 K) than the previous temperature (473 K) with the heating rate of 300 K/h. The accumulated gases were then measured by the same method. This step was repeated every 100 K up to 1273 K. In the higher temperature range of 1373–1873 K, an alumina tube was used, and the evolved gases were measured by the same way.

Fourier-transform infrared (FT-IR) spectra of the cured PVS after heat treatment in argon gas atmosphere were recorded by KBr method (FT/IR-5300, JASCO).

Thermogravimetric analysis (TGA) of the cured PVS from room temperature to 1273 K was conducted (TGA-50, Shimadzu). The hating rate was 5 K/min, and the atmosphere was nitrogen.

The density of the cured PVS after heat treatment in argon gas atmosphere was measured at room temperature by floating method using a solution of diiodomethane (density: 3330 kg/m^3 at 293 K) and chloroform (density: 1490 kg/m^3 at 293 K), or diiodomethane and N,N-dimethylformamide (density: 940 kg/m^3 at 293 K). The density was determined by averaging measured results of three specimens.

The microvickers hardness of the pyrolyzed PVS was measured using a microhardness tester (DUH-50, Shimadzu) that was fitted a micro-vickers indenter under a load of 0.49 N for 30 s. The microvickers hardness was calculated using following equation:

$$Hv(GPa) = 1.78 \times 104 \times P/d2$$

where P is the load (N) and d is the average length of the two diagonals (µm). The sample was embedded in an epoxy resin, and abraded by diamond slurry (0.3 µm finish). The hardness was measured at 20 points for one sample, and averaged.

Results and discussion

Ceramization process of γ-ray cured PVS

When the γ-ray cured PVS is pyrolyzed, decomposition gases are evolved as shown in Fig. 2. The gas evolution started above the temperature of 500 K, and hydrogen (H_2), methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), and ethane (C_2H_6) gases were detected. The H_2 gas evolution showed two peaks at around 700 and 1000 K. Such two peaks are attributed by the difference of covalent bonding energy of Si–H (318.0 kJ/mol) and C–H (410.5 kJ/mol) [9]. That is, the H_2 gas is evolved predominantly by cleavage of Si–H bonds in the lower temperature range, and by cleavage of C–H bonds in the higher temperature range. The H_2 gas was detected even at 1273 K, this suggests that the ceramization of PVS is not completed at this temperature. For the hydrocarbon gases, C_2H_4 gas evolved at 600–800 K, C_2H_2 and C_2H_6 gases evolved at 700–1000 K, and CH_4 gas evolved at 700–1100 K. These gases are considered to be evolved by decomposition of main chain or branch groups of the PVS.

Figure 3 shows the change of FT-IR spectrum of γ-ray cured PVS by heat treatment. For the unirradiated PVS, the absorbing peaks assigned to C–H stretching (2950, 2900 cm^{-1}), Si–H stretching (2100 cm^{-1}), Si–H stretching in Si–H_2 and/or Si–H_3 (2145 cm^{-1}), C–H deformation (1460, 1410 cm^{-1}), CH_2 deformation in Si–CH_2–CH_2–Si (1130 cm^{-1}), CH_2 deformation in Si–CH_2–Si (1020 cm^{-1}), Si–H deformation in Si–H_2 (940, 867 cm^{-1}), and Si–H deformation in Si–H_3 (945, 837 cm^{-1}) were found. After the irradiation, the peak intensity of Si–H bond decreased. This indicates that the radiation induced crosslinking of molecules mainly occurs at the site of Si–H. When the cured PVS is heat-treated, the peaks due to the Si–H bond decreased, and disappeared at 873 K. After the heat treatment at above 873 K, the peaks due to –CH_2– (1000–1100 cm^{-1}) and Si–C (around 800 cm^{-1}) were shown. This suggests that the H_2 gas evolved at high temperature range of 700–1000 K is attributed by the cleavage of C–H bonds (see Fig. 2).

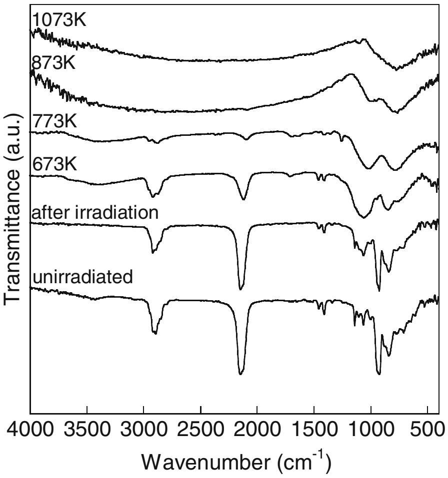

Fig. 3 Change of FT-IR spectrum of γ-ray cured PVS by heat treatment in Ar

Figure 4 shows the TG curve of γ-ray cured PVS from room temperature to 1273 K in N_2. In case of unirradiated PVS, the mass decreased drastically above 400 K, and the mass residue at 1273 K was 36%. On the other hand, in case of γ-ray cured PVS, the mass decreased drastically in the temperature range of 500–800 K, and the mass residue at 1273 K was 53%. Such increase in the mass residue is attributed by the crosslinking of molecules, and the mass residue increases with increasing in the dose of γ-ray irradiation. Large decrease of the mass in the temperature range of 500–800 K is considered to be caused by the gas evolution such as C_2H_4, C_2H_2, C_2H_6 (shown in Fig. 2), and the evaporation of low molecular weight components.

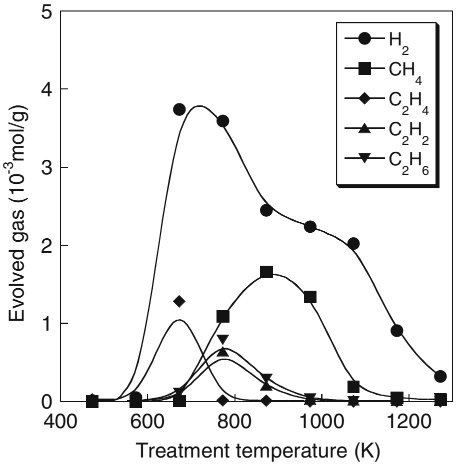

Fig. 2 Evolved gases from the γ-ray cured PVS by heat treatment

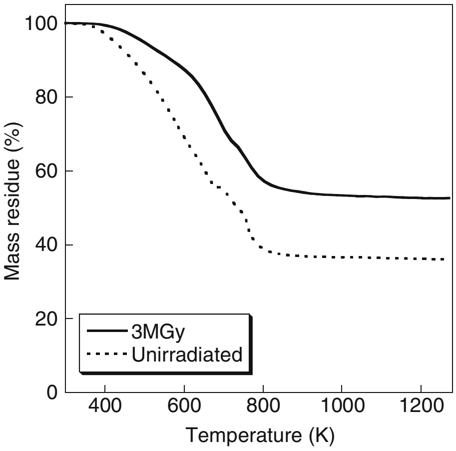

Fig. 4 TG curves of unirradiated and γ-ray cured PVS in N_2

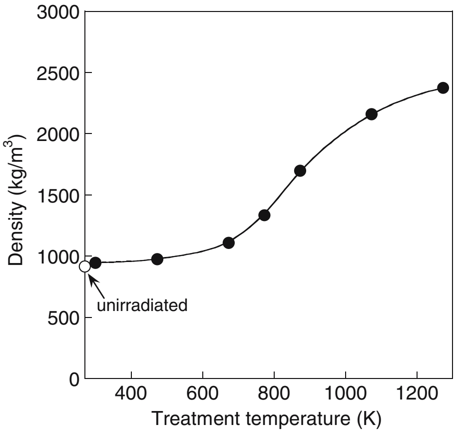

Fig. 5 Change of density of γ-ray cured PVS by heat treatment in Ar

The density of the unirradiated PVS is 915 kg/m^3. Figure 5 shows the change of density of γ-ray cured PVS by heat treatment in Ar. The density increased drastically in the temperature range of 700–1100 K, and it reached to 2370 kg/m^3 at 1273 K. According to the results of Figs. 2 and 3, the temperature range of 700–1100 K is the stage that 3-dimensional network is formed accompanied by much gas evolution. That is, the organic–inorganic conversion of the PVS occurs in this temperature range.

On the view point of size accuracy, it is important to estimate the volume shrinkage of PVS during the pyrolysis process. We examined a method to estimate the volume shrinkage from the results of the changes of mass and density of PVS during the pyrolysis process. Assuming that the primary volume of the PVS is 1 m^3, the relationship among the density, the mass residue after heat treatment, and the volume is represented by the following equation:

$$\mathrm{D}ensity(kg/m^3) = 915 \times Y(\%) \times 0.01/V(m^3)$$

where 915 is the density of unirradiated PVS, Y the mass residue after heat treatment, and V the volume of PVS after heat treatment.

Figure 6 shows relationship between relative volume of PVS estimated from equation described above and the treatment temperature. Not shown in Fig. 4, the mass of PVS decreased about 8% after the γ-ray irradiation, and the volume shrank about 10%. The volume decreased drastically in the temperature range of 500–1100 K, and the relative volume at 1273 K became 0.20. This suggests that the volume shrinkage of PVS in the radiation curing and the pyrolysis processes is 80%.

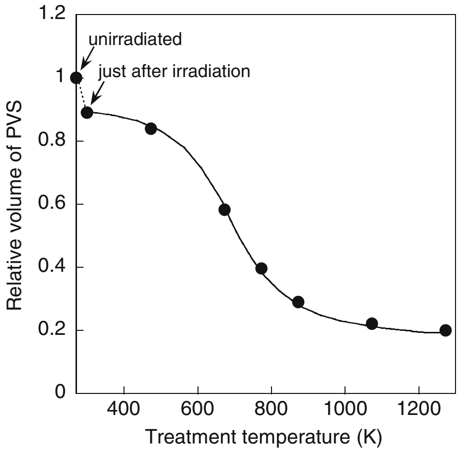

Fig. 6 Change of relative volume of PVS by heat treatment. The value was normalized by the volume of unirradiated PVS

The PVS was injected into a mold with 100 μm in square and 10 μm in depth, irradiated by γ-ray with dose of 3 MGy at room temperature under vacuum, and finally pyrolyzed at 1273 K in Ar. The obtained SiC minute products had the size of 60 μm in square and 5 μm in thickness (average of 3 specimens). The volume of the obtained SiC product is 18% for the capacity of the mold. This indicates that the result of calculation shown above is reasonable.

According to the results mentioned above, the ceramization process of the γ-ray cured PVS starts above 500 K, and organic–inorganic conversion occurs drastically in the temperature range of 700–1100 K. And, it was found that the volume shrinkage of PVS during radiation curing and pyrolysis processes is 80%.

Pyrolysis of γ-ray cured PVS at high temperature

As mentioned in the previous section (seen in Fig. 2), the ceramization of γ-ray cured PVS is not completed by the pyrolysis at the temperature of 1273 K. Then, the γ-ray cured PVS was pyrolyzed at higher temperature. Figure 7 shows the evolved gases from the γ-ray cured PVS by heat treatment at the temperature range of 1373–1873 K. While the amount of the H_2 gas evolution decreased with the increasing in the treatment temperature, it was detected even after the heat treatment at 1873 K. This is considered to be caused by that the C–H bonds are hardly decomposed due to the formation of 3-dimensional network of Si–C.

In order to fabricate the SiC minute products with high performance, it is important to reduce the –H groups in the structure as possible. For example, tensile strength of a SiC fiber which is synthesized from polycarbosilane with radiation curing increases as the

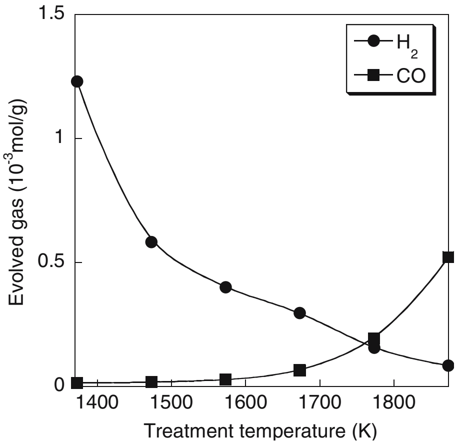

Fig. 7 Evolved gases from the γ-ray cured PVS by heat treatment in the temperature range of 1373–1873 K

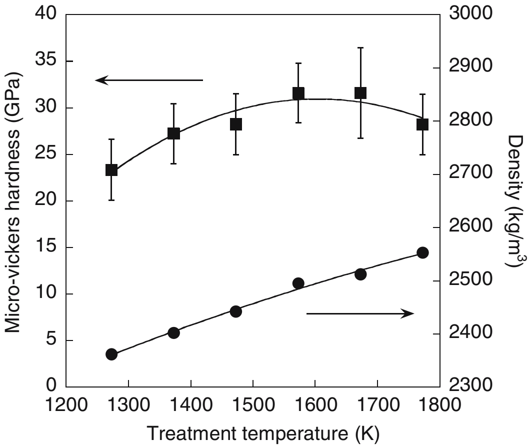

Fig. 8 Change of microvickers hardness and density by heat treatment in Ar

amount of H_2 gas evolution decreases [10]. We think that it is useful to make the heating rate slower in the temperature range of 700–1100 K in order to decrease the residual –H groups.

On the other hand, carbon monoxide (CO) gas evolution was found above the treatment temperature of 1673 K. This suggests that oxygen is incorporated in the specimen, and the oxygen maybe incorporated during the handling of the specimen. Assuming that the incorporated oxygen is only used for the CO gas evolution and consumed completely by the heat treatment at 1873 K, the concentration of incorporated oxygen in the specimen is estimated to be 1 wt%.

Figure 8 shows the change of microvickers hardness and density by heat treatment in Ar. The density increased slightly with increasing in the treatment temperature, and reached to 2550 kg/m^3 at 1773 K. This is considered to be caused by reduction of –H groups and crystallization of SiC. However, the density of 2550 kg/m^3 obtained is lower than that of β-SiC single crystal (3166 kg/m^3). This is caused by that the SiC synthesized from PVS contains excess carbon. We have reported about the ceramization process of reflux-treated PVS [11]. The reflux treatment is one way to cure the PVS, where volatile components generated during heat treatment under an inert atmosphere are forced to return into the system and to react with the polymer again by reflux. The C/Si ratio of the SiC obtained with reflux treatment was 1.53–1.54. On the other hand, the C/Si ratio of the SiC obtained without curing was 1.47. This means that the C/Si ratio does not depend on the curing treatment. Therefore, the C/Si ratio of the SiC obtained with radiation curing is considered to be about 1.5. The microvickers hardness increased with increasing in the treatment temperature, and showed the maximum average value of 31.6 GPa at 1573 K. However, the hardness decreased above the treatment temperature of 1773 K. This is considered to be caused by that the evolution of CO gas as shown in Fig. 7. The CO gas evolution is occurred by the reaction as follows [12]:

$$\text{Si-C-O (s)} \rightarrow \beta\text{-SiC(s)} + \text{SiO (g)} + \text{CO(g)}$$

This reaction makes the surface of the specimen so rough that the hardness decreased above 1773 K.

Conclusions

In this work, ceramization process of γ-ray cured PVS was investigated by gas analysis, TGA, density measurement, and so on. The following concluding remarks were obtained.

(1) The ceramization of γ-ray cured PVS starts above 500 K, and the drastic organic–inorganic conversion occurs in the temperature range of 700–1100 K.
(2) According to the changes of mass and density, it was found that the volume shrinkage of PVS during the curing and pyrolysis processes is 80%.
(3) The SiC obtained by pyrolysis at 1573 K in argon gas atmosphere showed the density of 2500 kg/m^3 and microvickers hardness of 31.6 GPa.

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