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Synthesis of a minute SiC product from polyvinylsilane with radiation curing

Part I *Radiation curing of polyvinylsilane*

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Irradiation effect of γ-ray on polyvinylsilane (PVS), which is a liquid organosilicon polymer, was investigated and the optimum curing condition to synthesize a minute SiC product with radiation curing was discussed. Room temperature and liquid nitrogen temperature (77 K) were examined as the irradiation temperature. In both cases, the cured PVS maintaining its formed shape could be obtained by γ-ray irradiation under vacuum, and the cured PVS in solid state at room temperature was obtained by irradiation with dose of above 3–4 MGy. It was found that the efficiency of crosslinking in case of the irradiation at room temperature is higher than that in case of irradiation at 77 K. The PVS injected into a mold was irradiated by γ-ray with dose of 3.6 MGy at room temperature under vacuum, and pyrolyzed at 1273 K in Ar gas atmosphere. As a result, minute SiC products which had similar shapes to the mold and the sizes of 30–60 μm were obtained.

1. Introduction

In the fields of aerospace technology and atomic energy development, the maintenance of equipments such as engines, cooling pipes, and so on, are indispensable for safe operation. However, inside of jet engines and inside of pipes in the nuclear power generator are hazardous environment such as high temperature, narrow space, and radiation. Therefore, it is important to develop a micromachine that conduct the maintenance of equipments in place of a human being, using microelectromechanical systems (MEMS) technology. In such a background, ceramic materials are more useful than polymers and metals because of their excellent mechanical properties, and thermal and chemical stability. Several researchers have reported about fabrication of minute ceramic products such as SiCN, ZrO_2, Al_2O_3, SiC, and SiOC for the applications for MEMS [1–6].

Silicon carbide (SiC), which has high strength, good thermal resistance, and stability against radiation or environment, is expected to be used as a structural material for heat resisting material of aerospace, and first wall of fusion reactor. If some parts of micromachines (bodies, gears, etc.) were made of SiC, a maintenance system which is available in hazardous environment could be realized. Furthermore, since the SiC is inert for the living things [7], an allergy-free medical catheter could be produced if a rotating blade for treatment in a blood vessel is made of SiC.

On the view point of fabrication of the ceramic products with the size ranging from several μm to several mm, the pyrolysis of preceramic polymers is a most advantageous method. Since the preceramic polymers have high formability, minute formed bodies with μm-order size or complex shapes are obtained easily. We have examined synthesis of a minute SiC product with the size ranging from several μm to several mm from preceramic polymer along the following process as one way: (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. It is useful to use a liquid preceramic polymer as a starting material in order to inject the polymer into the mold with μm-order size. Thus, polyvinylsilane (PVS), which is a liquid organosilicon polymer at room temperature, was selected as the starting material in this work.

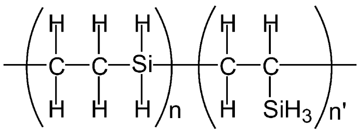
The curing treatment is necessary to synthesize a SiC product from the PVS, because a SiC maintaining its formed shape can not be obtained when the PVS is pyrolyzed without curing treatment. Generally, the curing treatment of the preceramic polymer is conducted by heat treatment. However, the PVS is thermally degraded above 500 K in argon gas atmosphere. While a reflux heat treatment is effective for the curing of PVS, it is necessary to conduct the heat treatment above 550 K [8]. On the other hand, in case of the radiation curing, it is possible to conduct the curing treatment at around room temperature, and furthermore, the irradiation conditions such as atmosphere, dose rate, dose, and so on, can be controlled optionally. Therefore, the radiation curing is advantageous over the heat treatment, and is adopted for the curing of PVS in this work.

In this paper, irradiation effect on the PVS was investigated, and the optimum condition for the curing of PVS in order to synthesize a minute SiC product was discussed.

2. Experimental procedure

2.1. Material

Polyvinylsilane (PVS) is synthesized by radical polymerization of vinylsilane ($CH_2{=}CHSiH_3$) in an autocrave using azobis(isobutyronitrile) [9]. It is a viscous liquid polymer with viscosity of about 200 $mPa \cdot s$ 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. The chemical structure of PVS is shown in Fig. 1. The unit ratio of n/n' is almost 1.



$$\left(\mathrm{CH_2{-}CH_2{-}SiH_2}\right)_n\left(\mathrm{CH_2{-}CH(SiH_3)}\right)_{n'}$$

Figure 1 Chemical structure of polyvinylsilane.

2.2. Irradiation of PVS

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 to dose of 15 MGy as maximum at liquid nitrogen temperature (77 K), and at room temperature under vacuum.

2.3. Measurements and analyses

The gases evolved from the PVS after the irradiation were analyzed by gas chromatograph (Gas Chromatograph 163, Hitachi). The measurement was conducted at room temperature. In case of the irradiation at 77 K, the specimen was heated to room temperature just after the irradiation.

Electron spin resonance (ESR) measurements for the PVS after the irradiation were conducted (JES-TE, Jeol). The free radical concentration was calculated from the spectral intensity by using $CuSO_4$ (1.53×10^{19} spins/g) as calibration. The measurements of the PVS irradiated at 77 K and at room temperature were conducted at 77 K and at room temperature, respectively. In case of the irradiation at 77 K, the irradiated PVS was heat-treated at melting point of several reagents such as ethanol (158.5 K), methanol (175.2 K), chloroform (209.5 K), carbon tetrachloride (249.2 K), and so on, and the change of the free radical concentration was investigated.

Gel fractions of the irradiated PVS were measured by using tetrahydrofuran (THF) as a solvent. The extraction time was 10 h, and the measurement was conducted at room temperature. The gel fraction was estimated by the equation as follows:

$$\text{Gel fraction(\%)} = [\text{Mass after extraction (g)}]/[\text{Mass before extraction (g)}] \times 100$$

The PVS after irradiation and pyrolysis at 1273 K in Ar gas atmosphere was observed by a digital microscope (VH-6300, Keyence) and scanning electron microscopy (JSM-5600, Jeol).

3. Results and discussion

3.1. Radiation curing of PVS

When the PVS was irradiated by electron beam (2 MeV of accelerating voltage, 972 kGy/h of dose rate, and 3 MGy of dose) at room temperature under vacuum, the PVS was foamed and solidified, as shown in Fig. 2a. This indicates that the cured PVS maintaining its formed shape can not be obtained in this condition. Such foaming is considered to be caused by that gas evolution and crosslinking of molecules occur simultaneously during the irradiation, as discussed in the next section. That is, the evolved gases by the irradiation are remained inner the specimen due to sudden crosslinking of molecules. There, the PVS was irradiated by ^{60}Co γ-ray (30 kGy/h of dose rate) with intension to reduce the rate of crosslinking during the irradiation. Although some specimens were foamed and solidified after the irradiation same as the electron beam irradiation, specimens which have large surface area (Fig. 2b and c) or small aspect ratio (Fig. 2d and e) are cured without foaming and maintain their formed shapes. That is, if the gases evolved during irradiation can come out of the specimen, it is possible to prevent the foaming of PVS.

On the other hand, the PVS was irradiated in the state of freeze by using liquid nitrogen with intension to suppress the gas evolution during the irradiation. In this case, the foaming of the PVS such as in the case of electron beam irradiation did not occur, and the cured PVS in solid state at room temperature was obtained not depending on the shape of specimen. Since the irradiation effect on the polymers such as polyethylene, polypropylene, and so on, is almost same between γ-ray and electron beam [10], the irradiation at liquid nitrogen temperature (77 K) is considered to be useful in the case of the curing of PVS by electron beam irradiation. And this may lead the irradiation time to be short.

According to the results mentioned above, it was found that the PVS can be cured without foaming by the γ-ray irradiation at room temperature or 77 K, and it is good to select the irradiation temperature depend on the shape of the specimen.

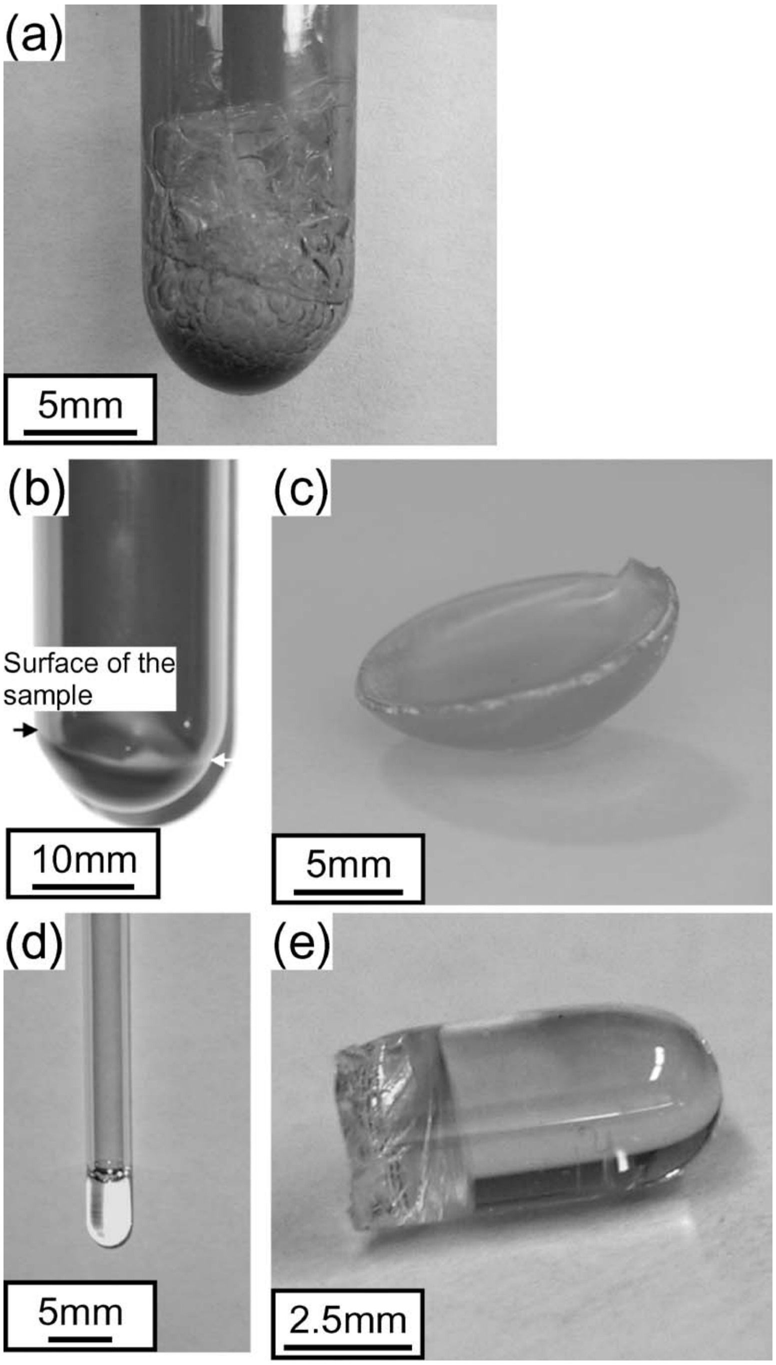


Figure 2 Photographs of PVS after irradiation: (a) PVS irradiated by electron beam (2 MeV of accelerating voltage, 972 kGy/h of dose rate) with dose of 3 MGy at room temperature under vacuum, (b), (c), (d), and (e) PVS irradiated by ^{60}Co γ-ray (30 kGy/h) with dose of 3 MGy at room temperature under vacuum ((b) and (c): 16 mm of inner diameter of glass tube, (d) and (e): 4 mm of inner diameter of glass tube).

3.2. Irradiation effect of γ-ray on PVS

Since it was found that the cured PVS without foaming could be obtained by γ-ray irradiation at room temperature and 77 K, the irradiation effect on the PVS was investigated in both cases.

Fig. 3 shows the evolved gases from the PVS after the γ-ray irradiation. The measurements were conducted at room temperature, and the gases measured in case of irradiation at 77 K are what evolved during heating up to room temperature. In both cases, hydrogen (H_2), ethylene (C_2H_4), methane (CH_4), and ethane (C_2H_6) were detected. The major gases were H_2 and C_2H_4, and occupied about 98% in molar ratio of the total gas. The H_2 gas is considered to evolve mainly due to scission of Si—H bonds, because the covalent bond energy of Si—H (318.0 kJ/mol) is lower than that of C—H (410.5 kJ/mol) [11]. The gases of hydrocarbons are considered to evolve due to scission of end groups or branch groups. In case of the irradiation at room temperature, the amount of evolved gases is more than that in case of irradiation at 77 K. This is because that the scission of bonds during γ-ray irradiation occurs more frequently at room temperature due to higher mobility of molecules compared with that at 77 K.

When the bonds are broken by γ-ray irradiation, free radicals are produced. They recombine each other, and the gases as mentioned above evolve. On the other hand, the free radicals trapped in the PVS recombine each other, and crosslinking of molecules occurs. However, the radicals, which do not contribute to crosslinking,

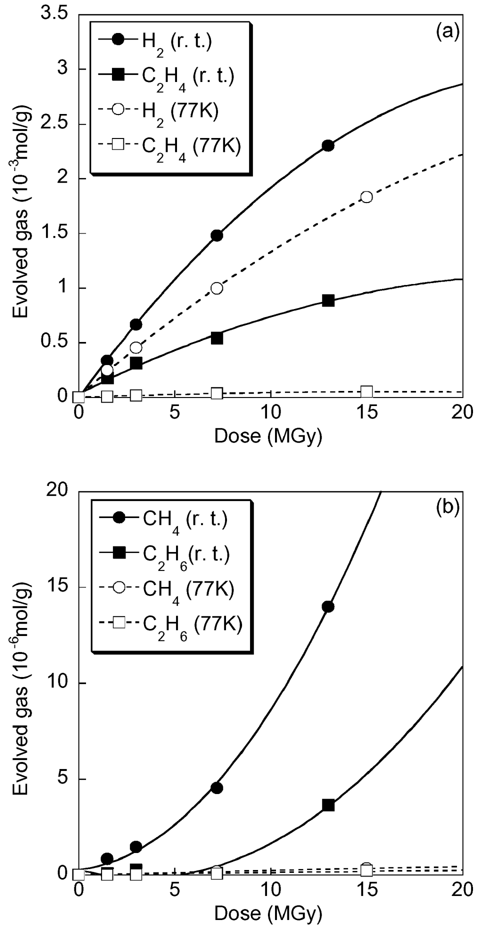


Figure 3 Evolved gases from PVS after γ-ray irradiation at room temperature and at liquid nitrogen temperature (77 K): (a) hydrogen and ethylene, and (b) methane and ethane.

are remained in the PVS. Such remaining radicals are needed to be vanished without exposing to the air, because they are easy to react with oxygen in the air [12]. Fig. 4 shows ESR spectra of PVS after γ-ray irradiation with dose of 7 MGy. In case of the irradiation at room temperature, the spectrum shows no peaks except for the peak due to quartz tube for ESR measurement (shown as "Blank"). This indicates that there is no remaining radicals in the irradiated PVS. That is, all of the radicals produced by irradiation recombine each other after the irradiation. This fact supports that the foaming of PVS as shown in Fig. 2a is caused by that the gas evolution and crosslinking occur simultaneously during the irradiation. Furthermore, this result means that the treatment to vanish the remaining radicals is not necessary in the case of irradiation at room temperature under vacuum. Therefore, the cured PVS can be pyrolyzed into the SiC product without any extra pre-treatment.

On the other hand, in case of the irradiation at 77 K, the spectrum shows a single broad peak with peak to peak width of about 3.4 mT. Such spectrum has been reported in the case of γ-ray irradiation for polycarbosilane (peak to peak width of 2.5 mT), whose chemical structure is represented as $\text{-(Si(CH}_3)_2\text{CH}_2)_m\text{-(Si(CH}_3)\text{HCH}_2)_{m'}\text{-}$, at 77 K under vacuum [12]. In this report, the broad peak has been considered to be consisted of Si radicals and C radicals. The PVS has Si—H, C—H, and Si—C bonds same as the polycarbosilane. Therefore, the remaining radicals in the PVS maybe also consisted of Si radicals and C radicals, and the

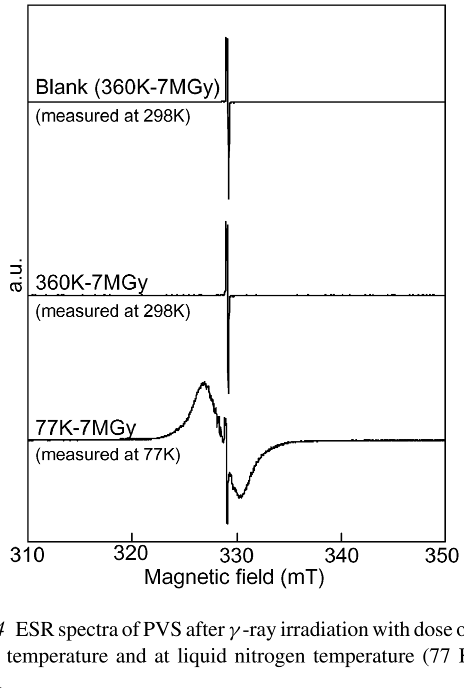


Figure 4 ESR spectra of PVS after γ-ray irradiation with dose of 7 MGy at room temperature and at liquid nitrogen temperature (77 K) under vacuum.

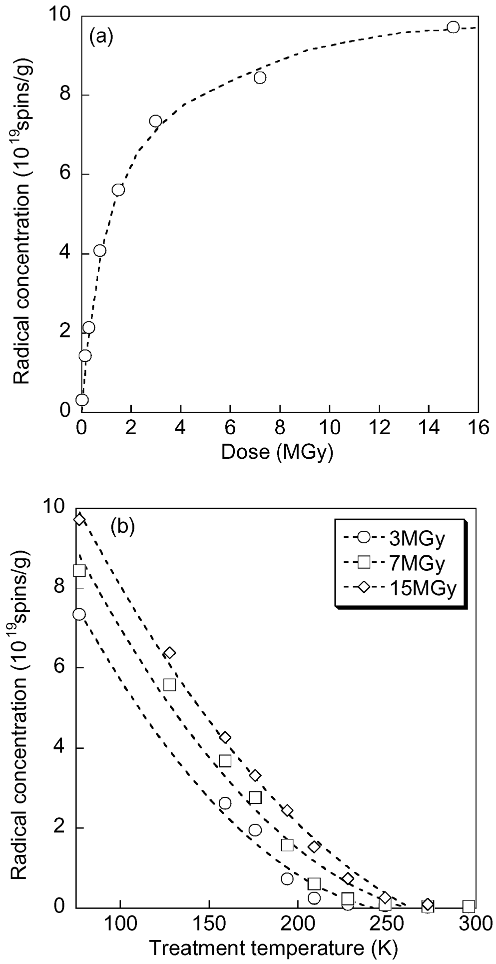


Figure 5 Results of ESR measurements of PVS irradiated by γ-ray at liquid nitrogen temperature (77 K): (a) free radical concentration in PVS after irradiation, and (b) change of free radical concentration by heat treatment.

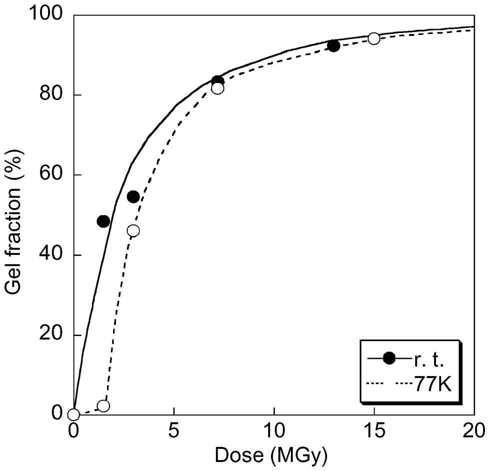


Figure 6 Relationship between dose of γ-ray irradiation and gel fraction of PVS.

broad peak may indicate that the environment around the radicals in the PVS is more complex than that in the polycarbosilane. The concentration of the remaining radicals in the PVS after irradiation increased with increasing in the dose, as shown in Fig. 5a, and is almost saturated above the dose of 10 MGy. However, not depending on the dose, the concentration of the remaining radicals was decreased by heat treatment, and it became almost negligible at the treatment temperature of about 270 K (Fig. 5b). This result means that the free radicals produced by γ-ray irradiation at 77 K under vacuum can be vanished completely by heating up to around room temperature.

Although the as-received PVS is soluble in the solvent such as benzene, tetrahydrofuran, and toluene, the PVS cured by γ-ray irradiation becomes insoluble in the solvent due to crosslinking of molecules. Fig. 6 shows the relationship between the dose of γ-ray irradiation and ratio of the insoluble component, that is, the gel fraction of PVS. The gel fraction was measured at room temperature. The gel fraction of PVS irradiated at room temperature shows higher than that of PVS irradiated at 77 K. At the dose of 1.5 MGy, the gel fractions are 50 and 2% in case of the irradiation at room temperature and at 77 K, respectively. This indicates that the efficiency of crosslinking in case of the irradiation at room temperature is higher than that in the case of irradiation at 77 K. This is caused by that the mobility of molecules at room temperature is higher than that at 77 K. The PVS with gel fraction of over 55% becomes solid. It is desirable to make the PVS solid in order to

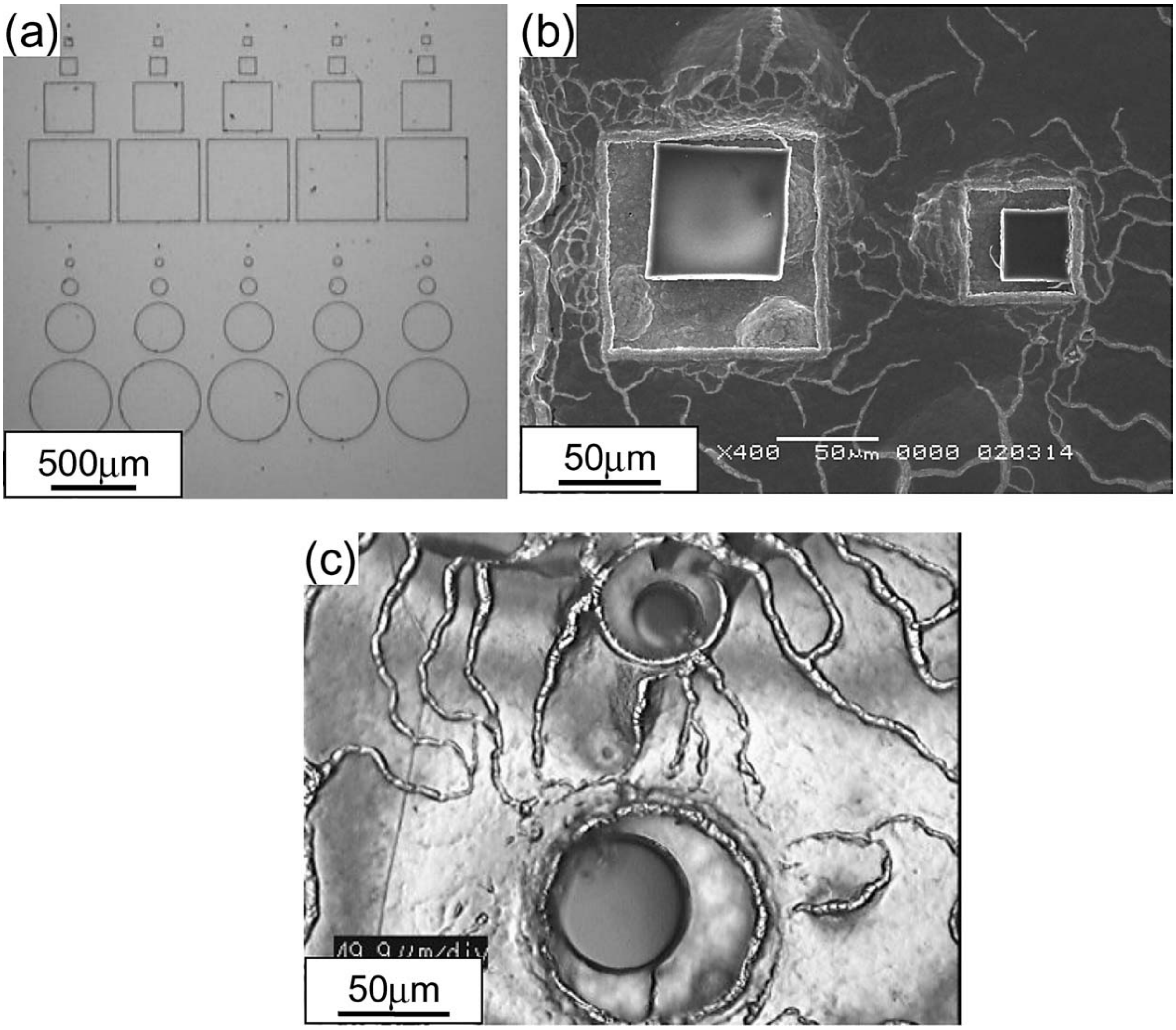


Figure 7 Photographs of minute SiC products synthesized from PVS with γ-ray curing: (a) mold which is made of nickel, and coated with rhodium (pattern depth of 10 μm), (b) and (c) obtained minute SiC products.

maintain the formed shape during subsequent pyrolysis process, therefore, the PVS is needed to be irradiated by γ-ray with dose of over 3–4 MGy.

According to the results mentioned above, it was concluded that the γ-ray irradiation at room temperature is advantageous in the curing process of the PVS if the foaming of the PVS does not occur. And, a solid cured PVS maintaining its formed shape is obtained by γ-ray irradiation with dose of above 3–4 MGy at room temperature under vacuum.

3.3. Minute SiC products synthesized from PVS with radiation curing

The PVS injected into a mold as shown in Fig. 7a was irradiated by γ-ray with dose of 3.6 MGy at room temperature under vacuum. After the irradiation, the cured PVS maintained its formed shape. The cured PVS was converted into the SiC products by pyrolysis at 1273 K for 1 h in Ar gas atmosphere (shown in Fig. 7b and c). The obtained SiC products had similar shapes to the molds. And the sizes of the products were about 30 and 60 μm in side or diameter, and about 5 μm in thickness. This result suggests that it is also possible to synthesize a minute SiC product with 2-dimensional complex shape such as a gear, in principle. The PVS is a very useful preceramic polymer to synthesize the minute SiC products.

4. Conclusions

In this work, irradiation effect on polyvinylsilane (PVS), which is a liquid organosilicon polymer, was investigated and the optimum curing condition to synthesize a minute SiC product with radiation curing was discussed. The following concluding remarks were obtained.

(1) The PVS is crosslinked and solidified maintaining its formed shape by the γ-ray irradiation with dose of 3–4 MGy under vacuum.

(2) In case of the irradiation at room temperature, the treatment to vanish the remaining free radicals in the PVS after irradiation is not necessary, because all of the radicals produced in the PVS recombine each other. Therefore, the cured PVS can be pyrolyzed into the SiC product without any extra pre-treatment. Even in the case of the irradiation at 77 K, the remaining free radicals can be vanished by heat treatment at about 270 K.

(3) Minute SiC products were synthesized from the PVS with γ-ray curing. The obtained SiC products had similar shapes to that of the molds, and the sizes of the products were about 30 and 60 μm in side or diameter, and about 5 μm in thickness.

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