Fine SiC fiber synthesized from organosilicon polymers: relationship between spinning temperature and melt viscosity of precursor polymers

A. IDESAKI, M. NARISAWA, K. OKAMURA
Department of Metallurgy and Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
E-mail: idesaki@taka.jaeri.go.jp

M. SUGIMOTO, S. TANAKA, Y. MORITA, T. SEGUCHI
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma 370-1292, Japan

MASAYOSHI ITOH
Material Science Laboratory, Mitsui Chemicals, Inc., Nagaura 580-32, Sodegaura, Chiba 299-0265, Japan

A very fine silicon carbide (SiC) fiber with diameter of 6 μm, about a half of that of a commercially available SiC fiber, was synthesized from a polymer blend of polycarbosilane (PCS) and polyvinylsilane (PVS). The fine SiC fiber was obtained by optimizing the composition and the spinning temperature of PCS-PVS polymer blends. In order to determine these optimum conditions, the relationship between temperature and melt viscosities of the polymer blends was investigated. As a result, it was found that the optimum spinning temperature range was within a temperature range where the melt viscosity is 5–10 Pa · s. Moreover, by blending PVS with PCS, the spinning temperature of the polymer blends was lowered, the spinnability of polymer system was improved, and finer polymer fiber was obtained compared with PCS. The optimum content of PVS in the polymer blend was 15–20 wt%. © *2001 Kluwer Academic Publishers*

1. Introduction

Silicon carbide (SiC) fiber, which has high tensile strength and good thermal resistance, is one of the most promising candidates as a reinforcement fiber of ceramic matrix composites (CMCs) for high temperature applications [1–3]. Usually, two or three-dimensional fabrics are used as reinforcements of the CMCs. In order to prepare such fabrics, it is important to develop a SiC fiber with small diameter, less than 10 μm, flexibility, and high strength. Chawla mentioned that for a SiC fiber with modulus of 420 GPa, it is required to decrease the diameter to 8 μm in order to show the same flexibility as that of Nylon fiber with diameter of 25 μm [4].

Generally, the SiC fiber is synthesized from polycarbosilane (PCS) as a precursor by melt-spinning, curing, and pyrolysis [5]. The diameter of commercially available SiC fibers is 12–15 μm. It is difficult to obtain finer SiC fibers because the spinnability of PCS is not so good and melt-spun PCS fiber is too brittle to process just after the melt-spinning. In order to improve the spinnability of the precursor polymer, we have blended polyvinylsilane (PVS) with PCS. The PVS is a viscous liquid polymer at ambient temperature and used as a spinning additive.

The melted precursor should be extruded out of the spinneret smoothly and drawn into a long fiber to obtain fine precursor fiber by melt-spinning. In this process, the relationship between spinning temperature and melt viscosity of the precursor polymer is very important. Hasegawa *et al.* measured the intrinsic viscosity of PCS, and found that molecular structure of the PCS is planar [6]. Toreki *et al.* conducted a dry-spinning of PCS at the viscosity of 25 Pa · s [7]. However, there is no report about the relationship between temperature and melt viscosity of the precursor polymers in order to find the optimum condition for synthesis of fine SiC fiber.

In this paper, the relationship between temperature and melt viscosity of the PCS-PVS polymer blend is investigated, and the optimum condition for the melt-spinning is found. As a result, a continuous SiC fiber of 6 μm in average diameter is obtained from the PCS-PVS polymer blend.

2. Experimental procedure

Polycarbosilane (PCS), supplied by Nippon Carbon Co., Ltd., is a solid polymer at ambient temperature, and has a number average molecular weight of 2.0×10^3. The chemical formula of PCS is represented as $[-Si(CH_3)_2CH_2-]_m[-SiH(CH_3)CH_2-]_{m'}$, and the unit ratio of m/m' is nearly equal to 1. Polyvinylsilane (PVS), supplied by Mitsui Chemicals, Inc., is synthesized by radical polymerization of vinylsilane ($CH_2{=}CHSiH_3$) in an autocrave [8]. The PVS is a viscous liquid polymer at ambient temperature, and has a number average molecular weight of 9.6×10^2. The chemical formula of PVS is represented as $[-CH_2CH_2SiH_2-]_n[-CH_2CH(SiH_3)-]_{n'}$, and the n/n' are nearly equal to 1. PVS contains no double bond in the structure, and is highly rich in Si–H bond compared with the PCS.

PCS-PVS polymer blends were prepared by freeze-drying of the benzene-polymer solution under vacuum. The PVS content in the polymer blends was changed from 5 to 40 wt%.

The PCS-PVS polymer blends were heated and held at a selected temperature ranging from 380 to 620 K for 30 min under N_2 gas atmosphere using a heater (Visco Block Model VTB-360S, Tohki Sangyo). Afterwards, the melt viscosities of the polymer blends were measured by a rotation viscometer (RB-80R, Tohki Sangyo).

The PCS-PVS polymer blends were melt-spun by a spinning apparatus built in our laboratory (Fig. 1). The polymer was put into the glass tube, and heated up to the melt-spinning temperature (PCS: 600 K, PCS-20%PVS: 490 K) under Ar gas atmosphere. And then, the elongated tip of the glass tube was broken to obtain a spinneret, and the extruded polymer fiber was wound onto a rotating drum. The diameters of the fibers were measured using a digital microscope (VH-6300, Keyence). The average diameter was determined from the measured results for 20 filaments.
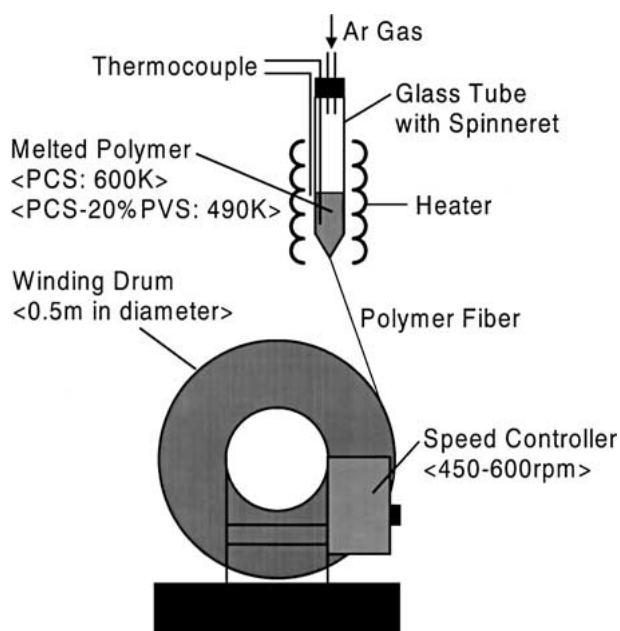
The as-spun polymer fibers were irradiated by 2 MeV electron beam with dose of 15 MGy under vacuum, and heated at 773 K for 30 min to quench active species produced by the irradiation. Finally, the cured fiber was pyrolyzed at 1473 K for 1 h under Ar gas atmosphere to obtain a SiC fiber. The obtained SiC fibers were observed by scanning electron microscopy (SEM: JSM-5600, JEOL).

The tensile strength of the SiC fiber was measured at room temperature using a tensile testing machine (Model-1305D, Aikoh Engineering) with a gauge length of 10 mm and a crosshead speed of 2 mm/min. The average tensile strength was obtained from the measured results of 20 filaments.

The density of the SiC fibers was measured at room temperature by floating method using a solution of di-iodomethane (density: 3330 kg/m^3 at 293 K) and chloroform (density: 1490 kg/m^3 at 293 K). The density was determined by averaging measured results of 3 filaments.

3. Results and discussion
3.1. Melt-spinning condition to obtain fine polymer fiber

In order to synthesize a finer SiC fiber from organosilicon polymer, it is necessary to prepare as fine a polymer fiber as possible. Since polycarbosilane (PCS) does not have good drawability in the melt state, we blended polyvinylsilane (PVS) as a spinning additive in order to obtain finer polymer fibers.

In the melt-spinning process, the spinning temperature of the polymer, the winding speed of the fiber, and the cooling temperature of the fiber are very important. The spinning temperature of the polymer is the most important among them, and there is a close relationship between temperature and melt viscosity of the polymer. Fig. 2 shows the relationship between temperature and melt viscosity of the PCS-PVS polymer blends. PCS, a transparent solid at ambient temperature, starts to soften at about 500 K, and its melt viscosity decreases abruptly with increasing temperature until around 580 K. Above 580 K, the melt viscosity hardly changes. In order to obtain fine polymer fiber by melt-spinning, the polymer must be drawn into a fine and long fiber when it is extruded out of the spinneret and
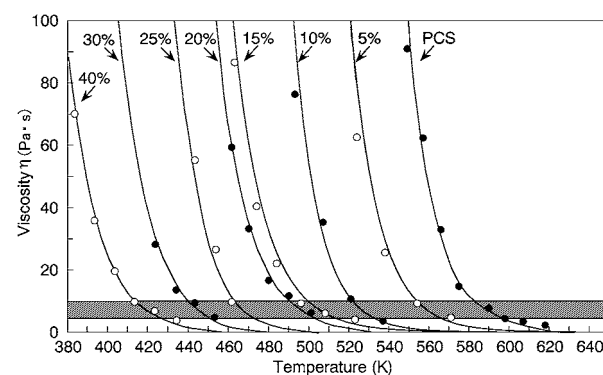

Figure 1 Scheme of melt-spinning apparatus for PCS-PVS polymer blends.

Figure 2 Relationship between temperature and melt viscosity of PCS-PVS polymer blends in N_2 gas atmosphere. Percentage is described as wt% of PVS in polymer blend.
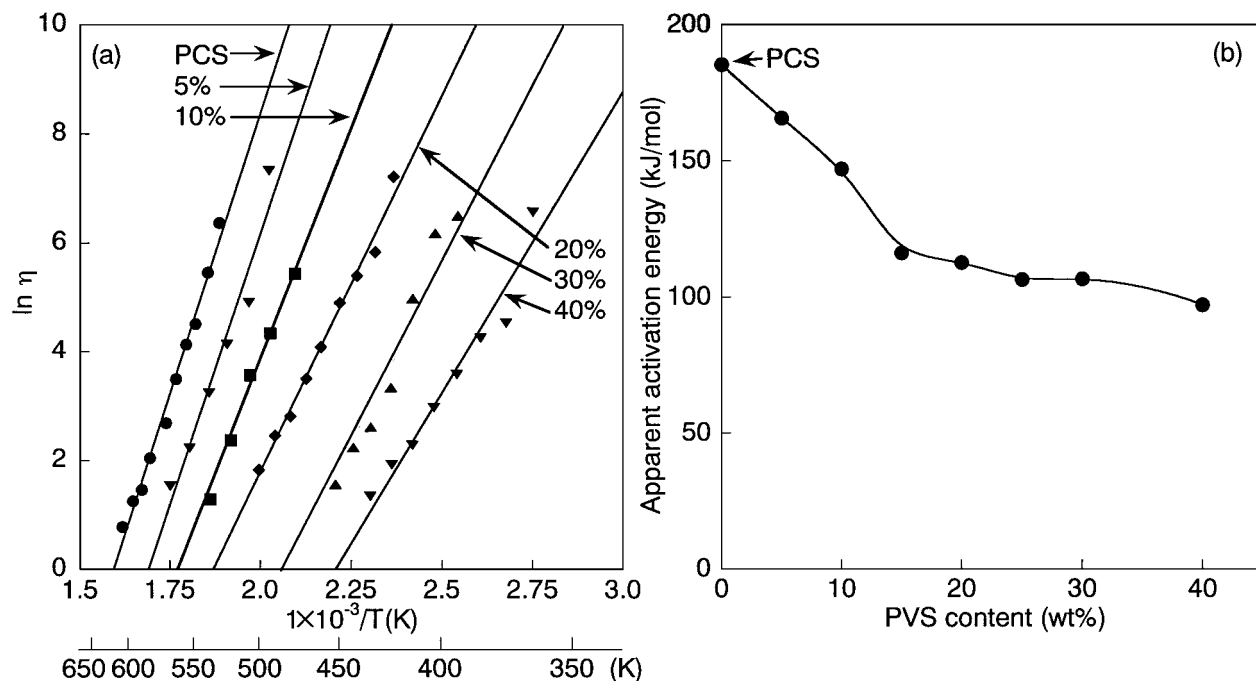
Figure 3 (a) Plots of ln η against $1/T$, and (b) relationship between PVS content and the apparent activation energy of PCS-PVS polymer blends.

wound onto the rotating drum, that is, before solidification from melting state with high fluidity. Therefore, the temperature of the polymer should be fixed within a temperature range where the polymer has high fluidity and constant viscosity. It was found experimentally that the optimum temperature for melt-spinning was within a temperature range where the melt viscosity is 5–10 Pa · s, as shown by the shaded area in Fig. 2. The polymer fiber often breaks at higher or lower temperature than this temperature range. The optimum temperature for the melt-spinning of PCS is about 600 K (Fig. 2). In the case of PCS-PVS polymer blends, the higher the PVS content, the lower the softening temperature of the polymer blends. Moreover, the curves of temperature-melt viscosity of the polymer blends are almost similar to each other. Therefore, the PCS-PVS polymer blends can be melt-spun in the same way as that for the PCS by merely lowering the temperature. The most suitable temperature for the melt-spinning is about 490 K for PCS-20%PVS, and about 440 K for PCS-30%PVS, which is more than 110 K lower than that for PCS.

The change of melt viscosity against temperature is approximated by following Andrade's equation [9, 10]:

$$\eta = A\, e^{U/RT}$$

$$\ln \eta = \ln A + U/RT \qquad (1)$$

where η is the viscosity, A is a constant, R is the gas constant of 8.531 J/K mol, U is an apparent activation energy for fluid per 1 mol (kJ/mol), and T is the absolute temperature. Fig. 3a shows plots of ln η versus $1/T$ for some typical polymer blends. The plots give straight lines and the slope becomes small as the PVS content increases, which means that the change of melt viscosity does not much depend on the temperature. The apparent activation energy for fluid, U, is obtained from the slope of the straight line of Fig. 3a according to

Equation 1. Fig. 3b shows the relationship between the apparent activation energy calculated and the PVS content. Comparing with the PCS, the activation energy of the PCS-PVS polymer blends decreases abruptly with increasing PVS content up to 15 wt%, and decreases gradually in the range of more than 15 wt% of PVS. By blending PVS, liquid polymer, with PCS, the mobility of the polymer system in the melt state increases, which is supported by the lowering of the softening temperature of the polymer blends (Fig. 2). As the mobility of the polymer system increases, the activation energy of the polymer system decreases.

Low activation energy of the PCS-PVS polymer blend indicates insensitivity of its melt viscosity change against temperature. In other word, the viscosity of the polymer blend increases more gradually during cooling down from the spinning temperature to ambient temperature compared with that of PCS in the melt-spinning process. Therefore, the polymer blend can be drawn into fine fiber without breaking. This indicates that the spinnability of the polymer system is improved by blending PVS with PCS. The PVS content required to lower the activation energy of the polymer system sufficiently is more than 15 wt% (Fig. 3b).

From the discussion described above, it can be said that the PVS lowers the melt-spinning temperature, and improves the spinnability of the polymer system, and that the PVS content required to lower the activation energy of the polymer system is more than 15 wt%.

3.2. Synthesis of fine SiC fiber
Fig. 4 shows diameter distributions of the polymer fibers obtained by melt-spinning. The average diameter of PCS fiber obtained was 11.8 μm at the finest, because the spinnability of PCS is not so good. In the case of the PCS-PVS polymer blends with PVS content less than 10 wt%, the spinnability of the polymer system was not improved enough to obtain fine polymer
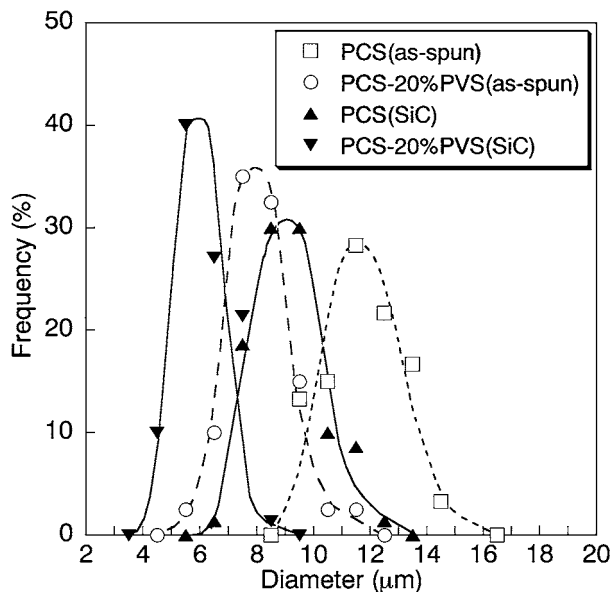
Figure 4 Diameter distributions of as-spun fibers and SiC fibers obtained from PCS-PVS polymer blend.

fiber. Fine polymer fibers were obtained from the polymer blends with PVS content over 15 wt%, and the average diameters of the polymer fibers were 8.4 and 8.2 μm for PCS-15%PVS and PCS-20%PVS, respectively. Such fine polymer fibers were obtained that did not break even when wound on the drum rotating at a linear speed of about 15 m/s in the melt-spinning process. In the case of the PCS, the maximum rotating speed was about 10 m/s. The reason for this good spinnability is that the apparent activation energy for fluid of the PCS-PVS polymer blends is lower than that of the PCS, as mentioned above (Fig. 3b). Low activation energy improves the spinnability of the polymer, and leads to finer polymer fibers from the polymer blends.

In the case of the polymer blends with PVS content of over 25 wt%, separated polymer fibers were not obtained because the fibers stuck to each other on the rotating drum during the melt-spinning process. It is expected that fine polymer fibers will be obtained if the

cooling condition is examined. However, it is very difficult to control the curing and pyrolysis conditions of these fibers due to their low softening temperature.

Based on the discussion described above, we may conclude that the PVS content of 15–20 wt% in the polymer blend is most suitable to obtain fine polymer fibers. In this work, the SiC fibers were synthesized from PCS and PCS-20%PVS. These polymer fibers were cured by electron beam irradiation with dose of 15 MGy under vacuum, and pyrolyzed at 1473 K for 1 h in Ar gas atmosphere. The SEM photographs of the SiC fibers synthesized are shown in Fig. 5. Both SiC fibers show smooth surfaces, and there is no difference in appearance.

The diameter distributions of the synthesized SiC fibers are also shown in Fig. 4. The polymer fibers are shrunk during the pyrolysis. While the average diameter of the SiC fiber from PCS is 9.1 μm, the SiC fiber from PCS-20%PVS has smaller average diameter of 6.0 μm. Moreover, the half width of the distribution curve at peak for PCS-20%PVS is about 70% of that for PCS. This is because the PCS-20%PVS was spun more stably in the melt-spinning process. The commercially available SiC fiber synthesized from PCS has average diameter of 12–15 μm [5]. By blending PVS with PCS, we could obtain fine SiC fiber with the diameter of about a half of that of the commercially available one. Such fine fiber is very flexible, therefore, it is expected that ceramic matrix composites with complex shapes can be more easily fabricated.

Table I shows the various properties of SiC fiber synthesized from PCS and PCS-20%PVS polymer blend. The tensile strengths of the SiC fiber from PCS and the polymer blend are 2.5 and 2.7 GPa, respectively. The yield of SiC fiber from the polymer blend is about 8% lower than that from PCS, because the amount of volatile products during the pyrolysis process from the polymer blend are more than that from PCS due to the lower molecular weight of PVS. However, it has been already found that the SiC yield from the polymer blend is increased up to about 80% by the electron beam curing with dose of 35 MGy under vacuum [11]. The density of SiC fiber from the polymer blend is 2330 kg/m^3,
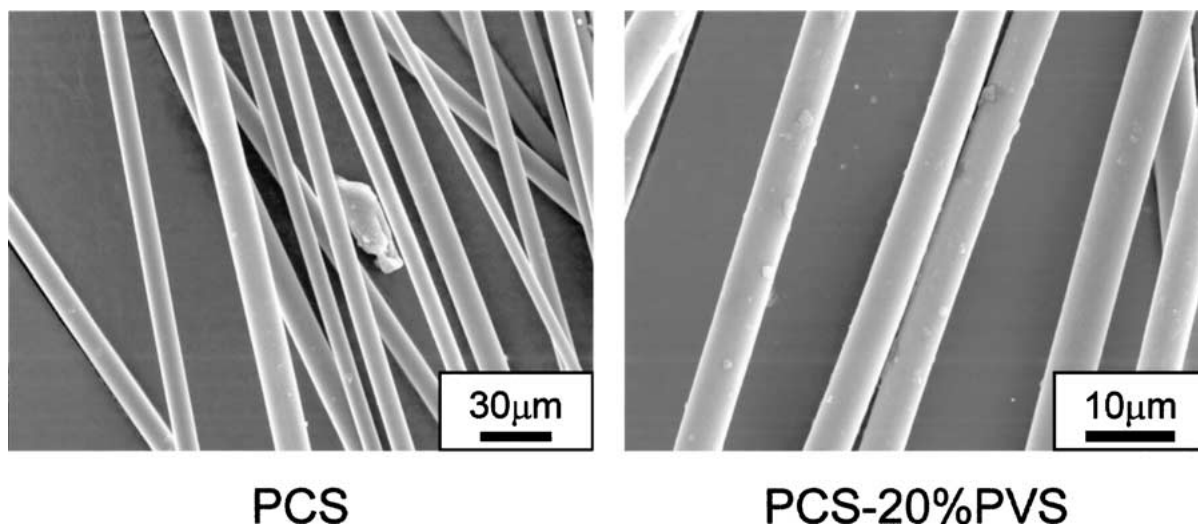

Figure 5 SEM photographs of SiC fibers synthesized from PCS-PVS polymer blends by electron beam curing with dose of 15 MGy under vacuum and subsequent pyrolysis at 1473 K for 1 h in Ar gas atmosphere.

Properties	PCS	PCS-20%PVS
Average diameter of		
as-spun polymer fiber (μm)	11.8	8.2
SiC fiber (μm)	9.1	6.0
Yield of SiC fiber[a] (%)	80.4	72.5
Average tensile strength (GPa)	2.5	2.7
Density[b] (kg/m^3)	2470	2330

Synthetic Condition: EB curing with dose of 15 MGy in vacuum, and pyrolysis at 1473 K for 1 h in Ar.

[a]Yield was estimated from weight ratio of SiC fiber/as-spun polymer fiber.

[b]Density was measured by floating technique.

which is slightly low compared with that of 2470 kg/m^3 from PCS. This seems to be caused by the same reason as that for the SiC yield. Low yield and low density indicate that structural defects are introduced into the SiC fiber synthesized from the polymer blend by the volatile products. The same applies to the SiC fiber from PCS. That is, a commercially available SiC fiber (Hi-Nicalon®) which is synthesized from PCS by electron beam curing has average diameter of 14 μm, tensile strength of 2.8 GPa, and density of 2740 kg/m^3 [5]. As the density (2470 kg/m^3) of the SiC fiber synthesized from PCS in this experiment is lower than that of Hi-Nicalon, the tensile strength (2.5 GPa) of the SiC fiber is lower than that (2.8 GPa) of Hi-Nicalon irrespective of smaller average diameter. This is considered to be caused by difference of the pyrolysis condition. Therefore, it is necessary to find the optimum pyrolysis conditions to suppress the volatile products and to increase the density of the fiber. After this optimization, the SiC fiber with small diameter and high tensile strength would be obtained in future.

4. Conclusions

In this paper, the most suitable condition for melt-spinning of PCS-PVS polymer blends was investigated from the view point of melt viscosity in order to obtain a fine SiC fiber. And the following concluding remarks were obtained.

1. The optimum temperature range for melt-spinning of PCS-PVS polymer blends can be determined by the relationship between temperature and melt viscosity of the polymer blends. The optimum temperature range for the melt-spinning is within a temperature range where the melt viscosity is 5–10 Pa · s.

2. By blending PVS with PCS, the spinning temperature is lowered, the spinnability of polymer system is improved, and finer polymer fiber is obtained. The optimum blending content of PVS in the PCS-PVS polymer blend is 15–20 wt%.

3. By optimizing the melt-spinning condition, very fine SiC fiber with the average diameter of 6 μm and the tensile strength of 2.7 GPa was synthesized from PCS-20%PVS polymer blend.

References

1. M. NARISAWA, T. SHIMOO, K. OKAMURA, M. SUGIMOTO and T. SEGUCHI, in "Fine Ceramic Fibers," edited by A. R. Bunsell and M. H. Berger (Marcel Dekker, New York, 1999) p. 207.
2. M. TAKEDA, A. URANO, J. SAKAMOTO and Y. IMAI, *J. Amer. Ceram. Soc.* **83** (2000) 1171.
3. M. SUGIMOTO, Y. MORITA, T. SEGUCHI and K. OKAMURA, in "High Temperature Ceramic Matrix Composites III," Key Engineering Materials Vols. 164–165, edited by K. Niihara, K. Nakano, T. Sekino and E.Yasuda (Trans Tech, Switzerland, 1999) p. 11.
4. K. K. CHAWLA, in "Composite Materials Science and Engineering" (Springer, New York, 1998) p. 6.
5. H. ICHIKAWA, *Bull. Ceram. Soc. Jpn.* **31** (1996) 662.
6. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **21** (1986) 321.
7. W. TOREKI, C. D. BATICH, M. D. SACKS, M. SALEEM, G. J. CHOI and A. MORRONE, *Comp. Sci. Tech.* **51** (1994) 145.
8. M. ITOH, K. IWATA, M. KOBAYASHI, R. TAKEUCHI and T. KABEYA, *Macromolecules* **31** (1998) 5609.
9. T. G. FOX, S. GRATCH and S. LOSHAEK, in "Rheology Theory and Application," Vol. 1, edited by F. R. Eirich (Academic Press, New York, 1956) p. 431.
10. E. N. DA C. ANDRADE, *Nature* **125** (1930) 582.
11. A. IDESAKI, M. NARISAWA, K. OKAMURA, M. SUGIMOTO, Y. MORITA, T. SEGUCHI and M. ITOH, *Rad. Phys. Chem.* **60** (2001) 483.