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Fiber reinforced plastics using a new heat-resistant silicon based polymer

M. ITOH
Chemistry and Biochemistry, Fukushima National College of Technology,
30 Aza Nagao, Taira Kamiarakawa, Iwaki-City, Fukushima 970-8034, Japan
E-mail: M-itoh@fukushima-nct.ac.jp

K. INOUE
Material Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagao,
Sodegaura-City, Chiba 299-0265, Japan

N. HIRAYAMA
Nittobo FRP Laboratory Co., Ltd., 1, Shiojima, Fukuhara, Fukushima-cho,
Koriyama-City, Fukushima 963-8061, Japan

M. SUGIMOTO, T. SEGUCHI
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy
Research Institute, 13 Watanuki-cho, Takasaki-City, Gunma, 370-1233, Japan

Fiber reinforced plastics (FRPs), reinforced with carbon fiber, SiC fiber and glass fiber, were prepared by using a new thermosetting silicon-containing polymer, poly[(phenylsilylene) ethynylene-1,3-phenyleneethynylene](MSP), as a matrix resin. In MSP composite processing, no solvent is needed, no by-products are generated, and the curing temperature is low (150–210°C). The FRPs (MSP composite) showed high heat-, burn- and radiation-resistant properties. Bending strengths (110–140 MPa) and modulus (30 GPa) at 200°C and 400°C were almost equal with those at room temperature, and were not affected by 100 MGy of irradiation. Dynamic viscoelasticity and creep properties of MSP composite were also determined and compared with those of a polyimide composite.

1. Introduction

Metals such as iron (specific gravity 8) and titanium (specific gravity 4.3) are highly heat-resistant and tough, however they have a high density. Ceramics, such as SiC, Si_3N_4, silica glass (SiO_2), are lighter (specific gravities 2–3) than most metals and highly heat-resistant, but have a lower toghness and are not as moldable. Many engineering polymers have been synthesized which are light (specific gravities 1–1.5), moldable, and have good mechanical properties relative to ceramics or metals. Polyimides have the highest heat resistance of all plastics, for example, Vespel (DuPont) has a heat distortion temperature (HDT: the temperature of a definite distortion under constant load and heating rate) of 360°C. Several polymers, such as polybenzyimidazol, polybenzothiazole, and polybenzooxazole, which have a higher heat resistance than the polyimides, have been developed, however, they are not moldable and are flammable. In general, an increase in the heat-resistance of a polymer is accompanied by the drastic lowering of the workability.

The goal of this research is to develop new materials that combine the best properties of plastics and ceramics. That is, the materials should have high heat- and burn-resistance like ceramics, and be as moldable and light as plastics. A potential candidate of this type of materials would be an organic polymer that is able to cross-link to form highly cross-linked structure near metals or ceramics. The chemical bonds Si—H, Si—Cl, Si—OR (R: alkyl or phenyl) and Si—Si are reactive; in particular, the Si—H bond reacts with many chemical bonds such as C≡C, C=C, CO, OH, NH, and C≡N. The Si atom forms thermally stable inorganic compounds such as SiC or SiO_2. Therefore, it is postulated that a silicon-based organic polymer is favorable for making such a material using a cross-linking reaction. On the basis of this concept, several polymers have been developed that contained a Si—H bond and another functional group in a molecule.

In our previous study, it has been determined that poly[(phenylsilylene)ethynylene-1, 3-phenyleneethynylene] (abbreviated as MSP), which is prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of magnesia [1, 2] or other base catalysts [3, 4] (see Fig. 1), has an extremely high thermal stability compared with the polyimides.

If MSP has a molecular weight (M_w) above 2000, it is a pale yellow and amorphous solid, and if it has a M_w under 2000, it is a viscous yellow liquid. The solid

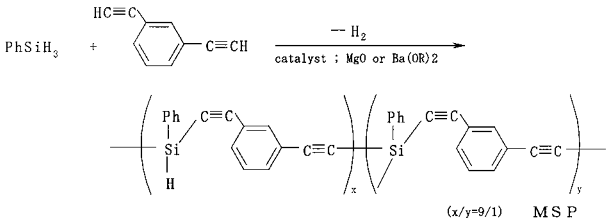

Figure 1 The reaction scheme for the preparation of MSP.

polymer is highly soluble in benzene, toluene, THF (tetrahydrofuran) and NMP (*N*-methyl-2-pyrrolidone). The glass transition temperature (T_g, determined by the differential thermal analysis (DTA)) of the polymer ($M_w = 5000 - 6000$) is about 50°C. The polymer is moldable, and it is possible to melt-spin the polymer at 100 –150°C. The polymers are stable for long periods under air. The color of the polymer gradually changes to black when cured above 150°C.

From the thermogravimetric analysis (TGA), there is very little weight loss during thermal cracking under argon. The Td_5 (temperature of 5% weight loss) is 860°C and the residue at 1000°C is 94%. These values are much higher than those of polyimide (Kapton; DuPont, Td_5 is 586°C and the residue at 1000°C is 55%). An exothermic peak at 210°C is observed in differential scanning calorimetry (DSC). This could be caused by intermolecular cross-linking reactions (curing reactions) between the Si—H bond and C≡C bond, which are addition reactions ($\text{—Si—H} + \text{—C≡C—} \rightarrow \text{—CH=C(Si)—}$) and produce no by-product [5]. No change in size of the molded test piece is observed up to 500°C. MSP is a insulator like other plastics and hard and fragile like glass.

The Td_5 (567°C) of MSP under air is nearly equal to that of Kapton (polyimide). The limiting oxygen indices (LOI: minimum oxygen concentration for the polymer to continue combustion) of MSP cured at 400°C and 500°C are 40–42 and 54, respectively (LOI of Vespel (polyimide) is 53). MSP is non combustible in air. In the flame produced by a gas burner, the molded MSP test piece turns red but does not burn and has no smoke. When the flame is removed, the test piece recovers its original black surface [6].

MSP has an extremely high ceramics yield (the residue at 1000°C is 94%). The specific gravity is 1.14 and constant in the range of 150°C to 500°C, and the value gradually increases above 500°C and the value at 1000°C is about 1.5, which is nearly equal to that of glassy carbon prepared from an organic compound such as phenol resin. The materials obtained by heating MSP at 1000°C or 2000°C for several hours under argon are glassy and hard. A molded block of MSP pretreated at 400°C contracts by about 10% in every dimension when heated at 1000°C and 2000°C for several hours. It is confirmed that the material is composed of carbon with silicon carbide particles (SiC 17–18%) from X-ray diffraction patterns, and Raman spectra suggest that the material is difficult to change into a crystal graphite [6, 7].

Many kinds of polyimides and phenolic resins have been developed as the matrix resin for FRPs [8]. They are generally soluble in only a polar solvent of high boiling point such as 1-methyl-2-pyrrolidone, dimethyl sulfoxide and *N*, *N*-dimethylformamide. In the case of the polyimides of the condensation type, the polyamic acids are used as precursors for molding, and be cured for a long time at high temperature (usually 300°C∼400°C) accompanied by the generation of water. It is necessary for the FRP to remove the water thoroughly to prevent any voiding. Therefore, it takes a long time to make a FRP.

In this study, we tried to prepare the new FRPs by using novel thermosetting resin "MSP" as the matrix resin, and carbon fiber, silicon carbon fiber or glass fiber as the reinforcement. The thermal and mechanical properties, dynamic viscoelasticity, and irradiation resistance were examined.

2. Experimental methods

In this section, the materials used for the FRPs, preparation methods of the FRPs, and the procedures for some characteristic evaluations of the FRPs are described.

2.1. Materials

Liquid MSP (Mw 820, Mn 540, viscosity 25 poise at 23°C, synthesized based on the previous report [2], was used as the matrix resin. Carbon fiber fabric (TORAYCA CO6343B made by Toray Industries Inc.), silicon carbide fiber fabric (NICALON NP1616 made by Nippon Carbon Co., Ltd.) and glass fiber fabric (Glass Cloth WF230 made by Nittobo Co., Ltd.) were used as the reinforcements. The specifications for the each fiber fabric are shown in Table I.

TABLE I Specifications of the FRPs using MSP, FRP (PMR-15) and silicon carbide

	Reinforcement						
Test piece		Weight (gm^{-2})	Thread count (25 mm^{-1})	Matrix	Content of reinforcement V_f (Vol%)	Number of plies	Thickness (mm)
CFRP	Carbon fiber fabric[a] TORAYCA CO6343B	198	12.5	MSP	44	9	2.0
SiCFRP	Silicon carbide fabric[a] NICALON NP1616	283	16	MSP	44	8	2.0
GFRP	Glass fiber fabric[a] Glass Cloth WF230	203	19	MSP	43	11	2.0
FRP (PMR-15)	Carbon fiber (unidirection)	–	–	Polyimide	60	15	2.2
SiC	–	–	–	Silicon carbide	–	–	2.0

[a] Plain fabric.

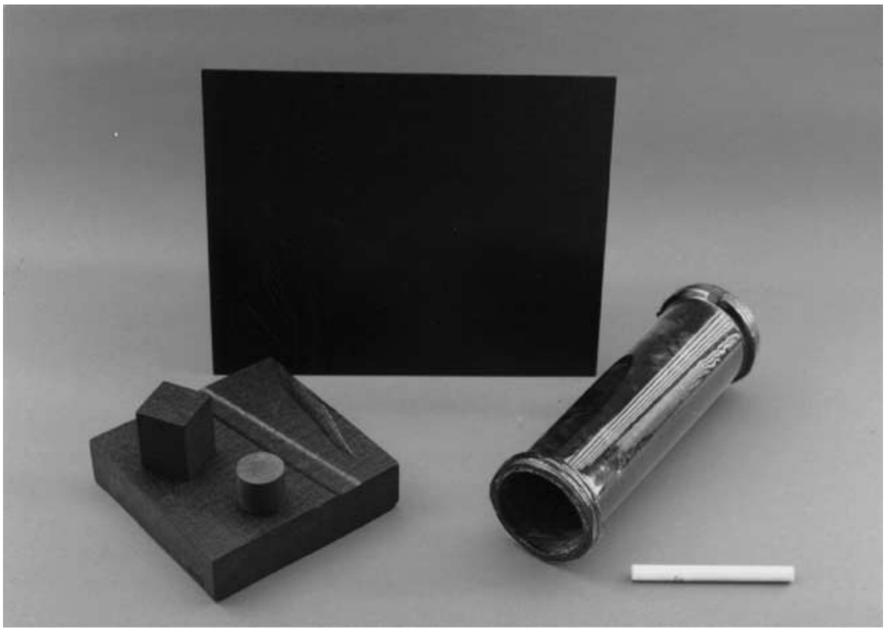

Figure 2 FRPs using MSP as a matrix resin.

2.2. Preparation of FRP

The prepreg was prepared by the following method. Each sheet of the fiber plain fabric was impregnated with the liquid MSP preheated at 100°C by the hand lay up method. Some impregnated sheets were then piled up, and excess liquid MSP and the bubble of the intercalation were pushed out at 100°C. In addition, the prepreg was pressed at 150°C for 12 hours under a pressure of 1.0 MPa by using the plane metal mold, and fiber content (V_f), which was determined from the weight content and the specific gravity of MSP, was 43–44 vol%. The numbers of the plies of the FRPs were 8–15 (see Table I). The FRP was cured under argon at 200°C, 400°C or 600°C for 2 hours before the evaluations of the characteristics of the FRP.

FRP was formed into pipe as shown in Fig. 2 in order to test whether a filament winding method was applicable. The carbon fiber was passed through the container including liquid MSP at 100°C, and the fiber impregnated with MSP was wound up on a metal mandrel. The metal mandrel was pulled out after curing at 150°C for 24 hours.

A FRP (Yokohama Rubber Co., Ltd.; abbreviated FRP (PMR-15)), which is prepared by using an unidirection carbon fiber and polyimide resin (PMR-15; developed by NASA-Lewis Reserch Center [9]), and a silicon carbide compact (Nikkato Co., Ltd.) was used for comparison. The specifications for the FRPs and comparison material are shown in Table I. CFRP, GFRP and SiCFRP indicate the FRP reinforced by carbon fiber, glass fiber and silicon carbide fiber, respectively.

2.3. Characteristics of the FRPs

2.3.1. Bending strength and modulus

The short term heat-resistant characteristics were evaluated by the bending strength and modulus at high temperature. The dimensions of the test piece were (b) 15 mm width, (l) 80 mm length and (t) 2 mm thickness, and all test pieces except for FRP (PMR-15) were cured at 400°C or 600°C under argon for 2 hours before the measurement to test the dependence on curing temperature. The tests were carried out under air at room temperature, 200°C and 400°C by using a universal test machine (DSS-10T-S made by Shimadzu Co. Ltd.) with an electric furnace. Five specimens were used for each test condition. The 3-point bending method was adopted and the distance (L) between supports was 60 mm. The temperature was measured by two thermocouples installed in the furnace and in the dummy material. The test was started after the dummy material reached the test temperature. The bending stress (σ_b) and bending modulus (E_b) were obtained according to equations:

$$\sigma_b = \frac{3FL}{2bh^2} \tag{1}$$

$$E_b = \frac{L^3}{4bh^3}\left(\frac{P}{\delta}\right) \tag{2}$$

F is the maximum load, and P/σ is an initial gradient of the test load-displacement curve.

2.3.2. Dynamic viscoelasticity

The dynamic viscoelastic properties were measured under air from room temperature to 500°C (2°C/min) by using a RSA II (DMA; Rheo Metrix Co., Ltd). The 3 point bending method was adopted and the distance (L) between supports was 50 mm, and the frequency was 1 Hz. The dimensions of the test piece were (b) 5–10 mm width, (l) 60 mm length and (t) 2 mm thick. MSP and the FRP using MSP were cured at 400°C under argon for 2 hours before the measurement.

2.3.3. Creep test

The long term heat-resistant characteristics were evaluated by the creep tests. The dimensions of the test pieces were 15 mm width, 80 mm length and 2 mm thick. MSP and the FRP using MSP were cured at 400°C under argon for 2 hours. The tests were carried out at 100°C and

200°C by using a tensile creep testing machine (CP5-L-200 type made by Orientic Co., Ltd.). The 3-point bending method was adopted and the distance (L) between supports was 60 mm. The test load (F) was 60% or 30–60% of the bending strength at 200°C in the silicon carbide compact and the other test pieces, respectively (see Fig. 7). The bending stress (σ_b) and the creep strain (ε_t) were calculated from Equation 1 and:

$$\varepsilon_t = \frac{6d_t h}{L^2} \qquad (3)$$

where F and d_t are the test load and creep deflection, respectively. The tests were carried out from 10 seconds to 100 hours, and the displacement of the load point was recorded.

2.3.4. Irradiation resistance

The FRPs reinforced by silicon carbide fibers were cut into test pieces of dimensions $b = 15$ mm width, $l = 80$ mm length, $t = 2$ mm thick. The test piece was installed in a sealed container and exposed to electron beam irradiation for a fixed time under a helium atmosphere (1.01×10^5 Pa). The electron beam energy was 2 MeV, the beam scanning width was 1.2 m, and the distance from beam window of the electron accelerator to the irradiation container base was 310 mm.

3. Results and discussion

There was little difficulty in fabricating the FRP laminates with the MSP resin (Fig. 2). Even if the FRPs were heat-treated in the temperature range of 200–600°C under nitrogen, there was no change in the appearance, except for the color change to black. Fig. 3 shows a section of a CFRP cured at 400°C. The fiber mat was well impregnated with MSP, but some bubbles and cracks were observed in the resin layer. The bubbles could be removed by using a resin transfer method (RTM) or autoclave method in mass-production. Further studies concerning the interface and adhesion between the fiber

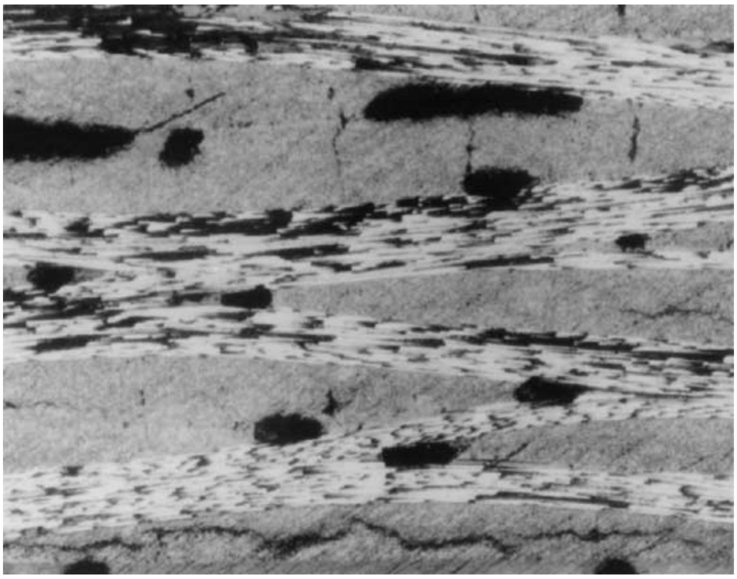

Figure 3 Section of CFRP cured at 400°C.

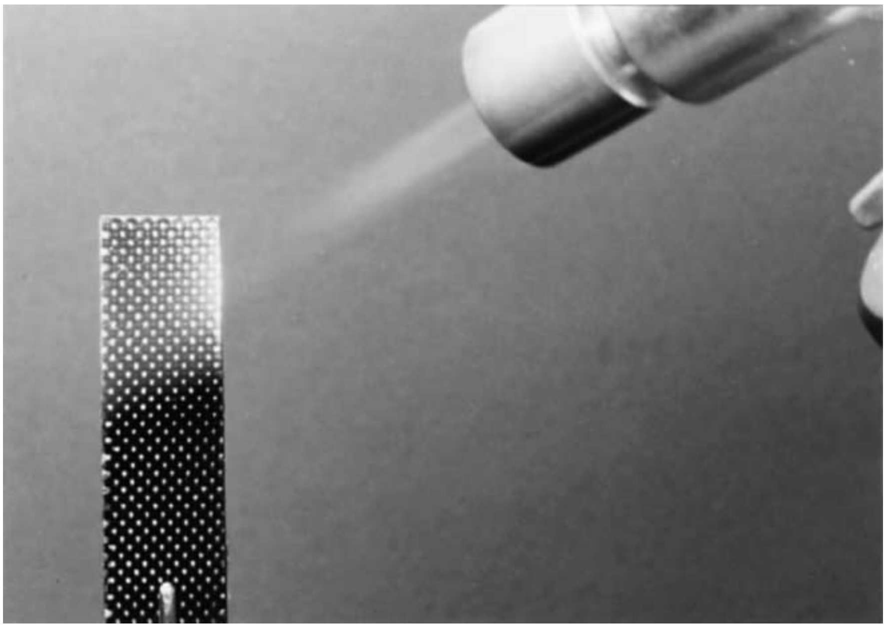

Figure 4 Combustion test of the CFRP using MSP. (non combustible and smokeless).

TABLE II Results of the tests bending strength and modulus of FRPs

Test piece	Curing temp. (°C)	Bending strength (MPa) 23°C	200°C	400°C	Bending modulus (GPa) 23°C	200°C	400°C
CFRP	400	111	120	142	31	33	35
CFRP	600	99	94	113	26	29	27
GFRP	400	80	79	95	14	13	13
GFRP	600	93	82	93	18	17	17
SiCFRP	400	110	111	110	30	29	30
SiCFRP	600	54	59	63	19	24	21

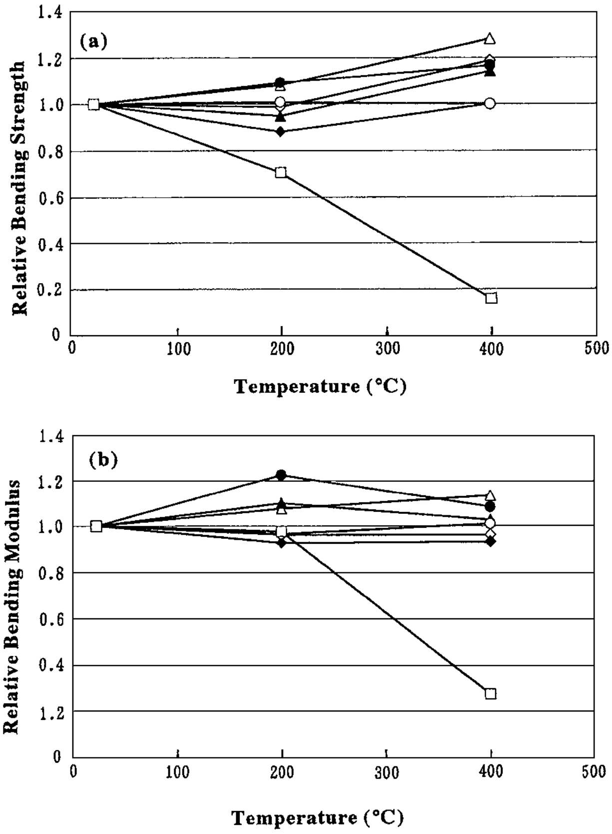

Figure 5 Changes of the bending strength (a) and modulus (b) with the measuring temperature. FRPs were cured at 400°C (opened mark) or 600°C (closed mark). (△) CFRP, (○) SiCFRP, (◇) GFRP, (□) FRP (PMR-15).

and MSP are needed to determine the optimum condition for the fabrication. The FRP was non-combustible in air. In the flame of a gas burner, the FRP turned red but did not burn and produced no smoke (Fig. 4) as in the case of the molded sample of MSP [6].

3.1. Bending strength and modulus

The bending strengths and bending moduli are shown in Table II, and the temperature dependence of the two values calculated from the data in Table II are shown in Fig. 5. The bending strength of the FRPs using MSP were lower compared to FRP (PMR-15), which could be caused by the voids and/or cracks in the FRPs.

The bending strengths and moduli of the FRPs using MSP as a matrix resin at room temperature, 200°C, and 400°C were almost equal, which suggests that the FRPs could be used even at 400°C, although further study of the mechanical properties at high temperature are needed. FRP (PMR-15), which contains the polyimide and carbon fiber, is one of the most heat-resistant FRPs and can be used at 300°C [8, 9]. Remarkable decreases in the strength and modulus were observed at 400°C in FRP (PMR-15), which could be caused by the thermal degradiation of the polyimide resin.

3.2. Dynamic viscoelasticity

Dynamic viscoelasticities of MSP, CFRP and FRP (PMR-15) are shown in Fig. 6. The storage modulus (E') and loss modulus (E'') of cured MSP were almost constant up to 500°C. The tan δ ($=E''/E'$), which is not shown in Fig. 6, was also almost constant. In the CFRP using MSP, E' was constant, whereas E'' decreased with increasing temperature. This could be caused by structural defects in the CFRP, such as an interlayer exfoliation, which would relate to the low bending strength of the CFRP. E' and E'' changed near 300°C in FRP (PMR-15), which could be caused by the thermal degradiation of the polyimide resin as in the case of the bending strengths and moduli.

3.3. Creep

The results of the bending creep tests at 100°C and 200°C are shown in Fig. 7. There was little creep in MSP, the CFRP using MSP and FRP (PMR-15) at 100°C similar to the silicon carbide compact. MSP, the CFRP using MSP and FRP (PMR-15) showed creep at 200°C. The creep strains of the CFRP gradually increased above 10 hours, and the values were higher than those of FRP (PMR-15). The changes of the creep strains of the CFRP at 100 hours under the test loads of 74 MPa and 37 MPa were 0.19% and 0.09%, respectively. The CFRP lacks a long-term heat-resistance under a load of about 30% of the static strength, though the CFRP using MSP had an excellent strength retention under 400°C (Fig. 5).

3.4. Radiation resistance

The bending strengths and moduli of a SiCFRP using MSP subjected to the electron beam irradiation are shown in Fig. 8. The bending strength and modulus of SiCFRP cured at 400°C did not change with 100 MGy of irradiation. The bending strength of the SiCFRP cured at 200°C was decreased by irradiation, which could be caused by the continued curing of the sample. The total amount of the irradiation is estimated to be 0.5 MGy in a light water reactor, and 50–100 MGy in a fast breeder reactor and a nuclear fusion reactor. It is known that mechanical characteristics decrease under

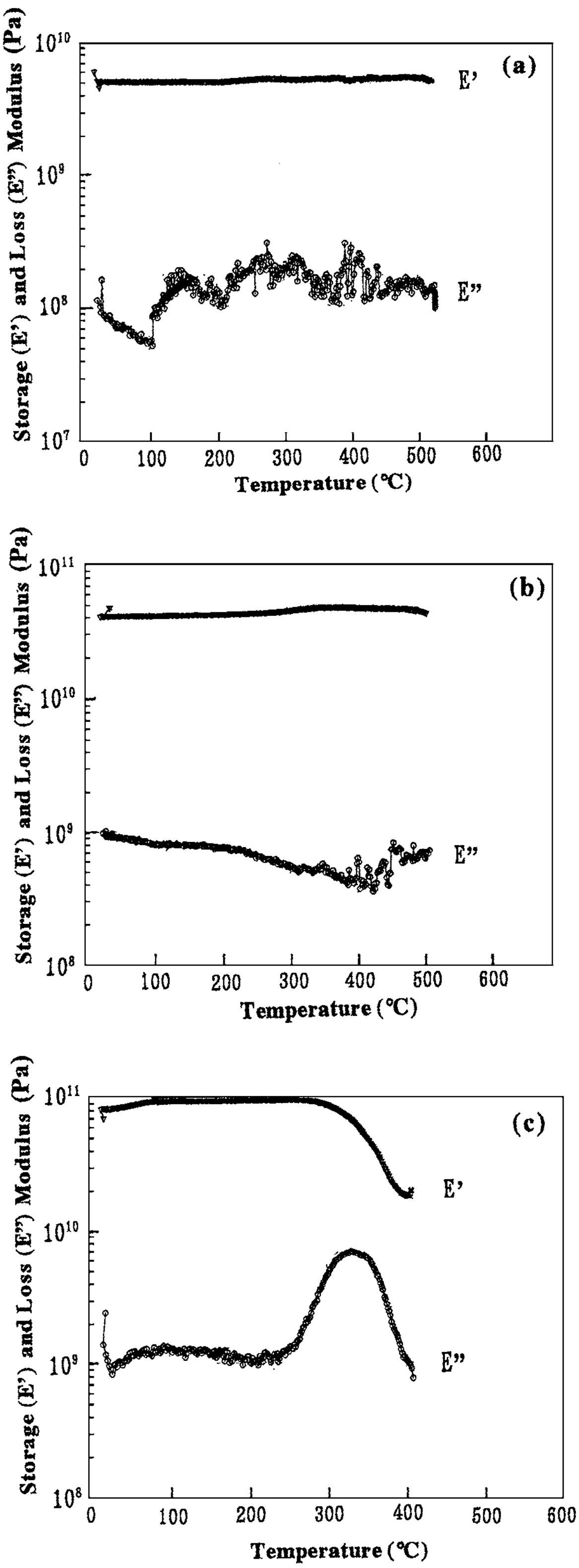

Figure 6 Dynamic viscoelasticities of MSP (a), CFRP (b) and FRP (PMR-15) (c).

irradiation in many engineering plastics, such as polyimide materials [10]. It is clear that the highly cured SiCFRP has a higher radiation resistance than the FRPs using many other engineering plastics. Cured MSP is surrounded by π electrons of the C≡C bond, the C=C bond produced by curing reaction and the phenyl group, and σ electrons of the silicon atom. The SiCFRP using MSP could show a high radiation resistance due to the shielding effects of these electrons.

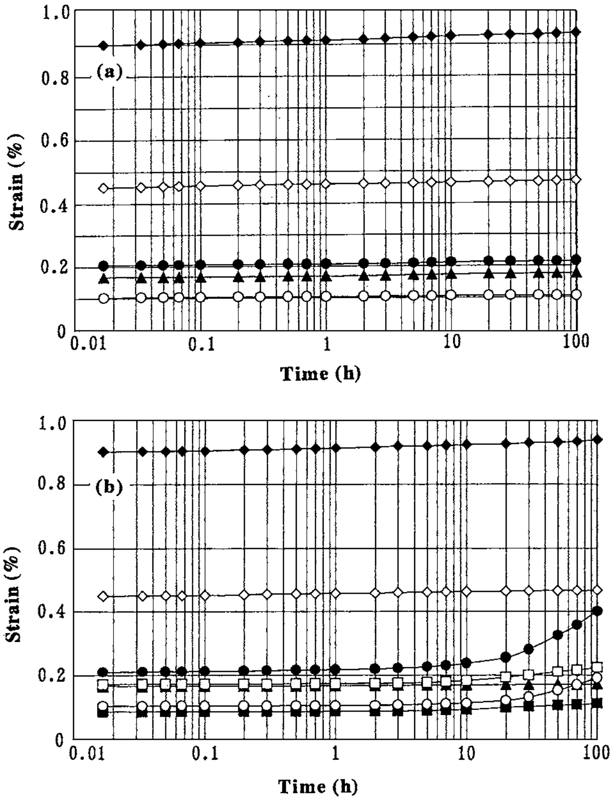

Figure 7 Bending creap test at 100°C (a) and 200°C (b). MSP (□: 10 MPa, ■: 5 MPa), CFRP (MSP) (●: 74 MPa, ○: 37 MPa) FRP (PMR-15) (◆: 639 MPa, ◇: 320 MPa), SiC (▲: 255 MPa).

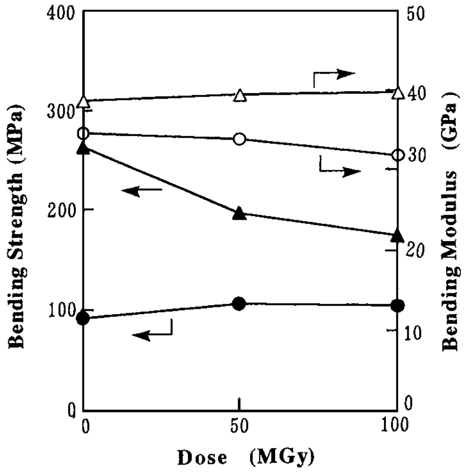

Figure 8 Radiation-resistant property of SiCFRP (MSP). (△, ▲): cured at 200°C for 2 hours, (○, ●): cured at 400°C for 2 hours.

4. Conclusion

This report introduces a new FRP using MSP, which is a silicon based thermosetting polymer, as a matrix. MSP is highly heat-resistant, nonflammable, and has a reactive Si—H bond which is able to create bonds with many reinforcing materials. Moreover, MSP is moldable, soluble in many solvents of low boiling-point, and can be cured at low temperatures with no generation of a by product. When an oily oligomer is used, no solvent is needed. These characteristics of MSP are superior to those of polyimides in preparing fiber reinforced materials.

FRPs were prepared using MSP and glass, carbon and silicon carbide fibers. The FRPs have reasonable mechanical strength at 400°C in air and showed high radiation resistance. There was little creep at 100°C, however, significant creep was observed at 200°C in the FRP using MSP. A limit to the long-term heat-resistance was suggested.

By using the high heat-, burn- and radiation resistant properties of MSP, some materials of the FRPs have been applied. An ablation material and a nozzle of a rocket motor in aerospace plane are under testing [11]. Moreover, MSP has a high residue at elevated temperature (the residue at 1000°C is 94%). Application to C/C composite and functionally gradient material (FGM) are also under studying.

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