Advanced Composite Materials

Carbon fiber reinforced composites with newly developed silicon containing polymer MSP

T. Ogasawara , T. Ishikawa , M. Itoh , T. Abe , R. Yokota & M. Ando

Version of record first published: 02 Apr 2012.

To cite this article: T. Ogasawara , T. Ishikawa , M. Itoh , T. Abe , R. Yokota & M. Ando (2001): Carbon fiber reinforced composites with newly developed silicon containing polymer MSP , Advanced Composite Materials, 10:4, 319-327

To link to this article: http://dx.doi.org/10.1163/156855101753415346

Adv. Composite Mater., Vol. 10, No. 4, pp. 319–327 (2001)

Carbon fiber reinforced composites with newly developed silicon containing polymer MSP

T. OGASAWARA [1,*], T. ISHIKAWA [1], M. ITOH [2], T. ABE [3], R. YOKOTA [4] and M. ANDO [5]

[1] *National Aerospace Laboratory of Japan, 6-13-1, Ohsawa, Mitaka-shi, Tokyo, 181-0015, Japan*
[2] *Fukushima National College of Technology, 30, Aza Nagao, Taira Kamiarakawa, Iwaki-shi, Fukushima 970-8034, Japan*
[3] *Mitsui Chemicals, Inc., Sodegaura-shi, Chiba, 299-0265, Japan*
[4] *Institute of Space and Astronautical Science, Sagamihara-shi, Kanagawa, 229-8510, Japan*
[5] *Toho Tenax Co., Ltd., Nagaizumi-cho, Shizuoka, 411-8720, Japan*

Abstract—The objective of this study is to investigate the processing, material characteristics and mechanical properties of carbon fiber reinforced composites with newly developed silicon containing polymer. The polymer, poly[(phenylsilylene) ethynylene-1,3-phenyleneethynylene], abbreviated MSP, possesses low thermosetting temperature (423–480 K), no volatility with cure, excellent heat-resistance and high char yield above 1273 K. In this study, carbon fiber reinforced composites with MSP were made by prepreg consolidation with plain 2D woven prepreg sheets, and resin transfer molding (RTM) with stitched plain 2D woven preforms. Compressive tests were conducted in order to evaluate the mechanical properties of the composites. However, the strengths of the composites were poor at elevated temperature. It was attributed to embrittlement and shrinkage of the polymer during heat treatment above 473 K.

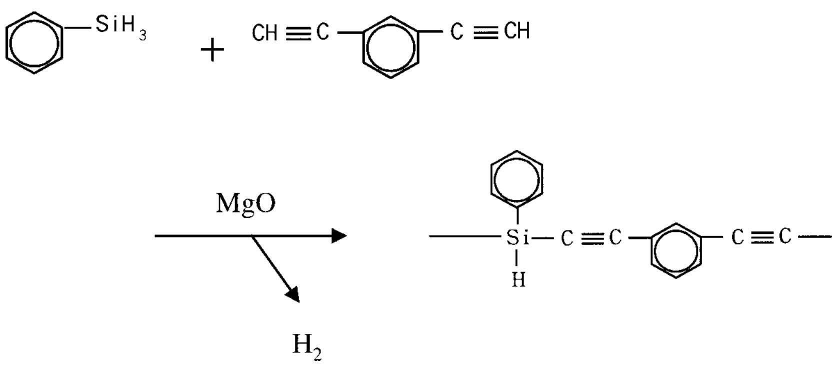
Keywords: Silicon containing polymer; high temperature; thermosetting; carbon fiber; prepreg consolidation; resin transfer molding; compressive strength.

1. INTRODUCTION

The polymer, poly[(phenylsilylene) ethynylene-1,3-phenyleneethynylene] (abbreviated MSP), was developed by Mitsui Chemicals Ltd. in 1994 [1]. The polymer is made by dehydrogenative coupling polymerization reactions between phenylsilane and *m*-diethynylbenzene (Scheme 1) [1, 2]. The polymer has reactive $-\mathrm{Si}-\mathrm{H}$ and $-\mathrm{C}{\equiv}\mathrm{C}-$ bonds, and it is cross-linked above 423 K by hydrosilylation reaction between $-\mathrm{Si}-\mathrm{H}$ and $-\mathrm{C}{\equiv}\mathrm{C}-$. The Diels–Alder reaction between $-\mathrm{C}{\equiv}\mathrm{C}-$ and

---

[*] To whom correspondence should be addressed. E-mail: ogasat@nal.go.jp.



Scheme 1.

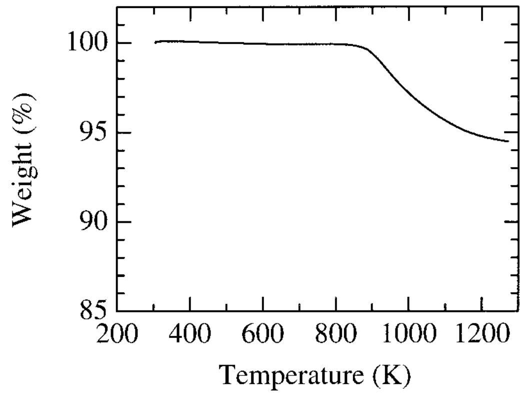


Figure 1. Thermogravimetric analysis (TGA) result of MSP polymer (type-S) in Argon atmosphere. Heating rate was 10°C/min, and gas flow rate was 300 ml/min.

—C≡C— proceeds above 473 K and a very highly thermally stable structure is formed. Thermogravimetric analysis result of cured polymer in argon atmosphere is shown in Fig. 1. The cured polymer has pyrolysis temperature in excess of 800 K, and high char yield (94% at 1273 K).

Engineering applications of MSP polymer have been studied for several years, such as fiber reinforced composites [3], glassy carbon [3, 4], electrical insulators and ablative materials [5]. MSP possesses some advantages as matrix material of high temperature polymer matrix composites compared to other high temperature polymers such as polyimides, because it has low thermosetting temperature (423–480 K), no volatility with cure, high decomposition temperature (>800 K) and high char yield after pyrolysis. However, few investigations on MSP matrix composites have been reported yet.

In this study, carbon fiber reinforced composites (CFRP) with MSP polymer matrix were fabricated by a prepreg consolidation method, and a resin transfer molding (RTM) method. MSP polymer was characterized using thermal analyses and FT-IR in order to establish processing conditions. Mechanical properties of composites were evaluated by compressive tests at elevated temperature as well as room temperature.

2. EXPERIMENTAL PROCEDURE

2.1. Polymer properties

Polymers used in this study were a pale yellow amorphous solid (type S) for prepreg preparation, and a viscous yellow liquid (type L) for an RTM fabrication. Weight-average molecular weight (M_w) of the polymers was 7420 for S-type polymer and 2120 for L-type polymer, respectively. Viscosity of L-type polymer was 10 Pa s at 323 K, and 1 Pa s at 363 K, which was low enough to apply the polymer to an RTM processing.

Chemical structures of the polymer were characterized using a Fourier transform infrared spectrometer (FT/IR-610, JASCO, Japan). Thermal expansion and shrinkage behaviors were evaluated by a thermal mechanical analyzer (TMA-6300, Seiko Instruments, Japan).

2.2. Kinetic analysis of cure

Kinetic analyses of cure process in epoxy resin have been reported many times based on a differential scanning calorimetry (DSC) technique [6]. The work is concerned with an estimation procedure for determination of kinetic parameters. It is assumed that rate of heat generation during cure is proportional to rate of cure reaction. In general, degree of cure C of polymer may be defined as:

$$C = H(t)/Q,$$

where $H(t)$ is the heat evolved from the beginning of reaction to final time, and Q is the total or ultimate heat generation during cure. Reaction of thermosetting polymer systems can be realistically assumed by the following kinetic expression:

$$\mathrm{d}C/\mathrm{d}t = k(T)f(C),$$

where, C is the degree of cure, T is the temperature, t is time, $k(T)$ is the reaction rate constant expressed as a function of temperature, and $f(C)$ is the equation as a function of C dependent on type of reaction. Simple equations for $k(T)$ and $f(C)$ can be expressed as follows:

$$k(T) = A\exp\{-(E/RT)\},$$
$$f(C) = (1 - C)^n,$$

where A is a constant, E is the activation energy, R is the universal gas constant (= 8.31 J/mole/K), and n is the reaction order. Using these equations, the degree of cure was modeled throughout the range of applicable temperature (25–773 K).

2.3. Processing and characterization of composites

Materials and processing parameters of the composites (MSP-CFRP) fabricated by prepreg consolidation method are listed in Table 1. MSP polymer/carbon fabric prepreg was formulated by a solution impregnation process using toluene as solvents. IM-600-6k plain weave fabrics (Toho Rayon, Japan) were used for reinforcement. Prepreg sheets were stacked by hand lay-up, and prepreg laminates were consolidated using a hot-press at 423 K for 3 h. By the prepreg consolidation technique, high quality composite laminates without voids were obtained.

The processing parameters of MSP matrix composites fabricated by an RTM method are listed in Table 2. IM-600-6k plain weave fabrics were stacked, and

Table 1.
Materials and processing parameters of MSP/CFRP fabricated by prepreg consolidation

Carbon fiber	IM-600-6k (Toho Rayon)
Carbon fabric	Fabric; plain weave (0°/90°) W6E01 Areal Weight; 200 g/m^2 Count warp and fill; 492 yarn/m
Polymer	MSP type-S (STM-3S, Mitsui Chemicals) Solid type, $M_\mathrm{n} = 3050$, $M_\mathrm{w} = 7417$
Polymer content	38 wt%
Fiber fraction	48–50 vol% ($x : y = 1 : 1$)
Ply	20 (Nominal thickness 4.5 mm)
Cure temperature	Pre-cure; 423 K, 3 h Post-cure; (a) 473 K, 2 h, (b) 673 K, 2 h
Fabricator	Toho Rayon Co., Ltd.

Table 2.
Materials and processing parameters of MSP/CFRP fabricated by resin transfer molding (RTM)

Carbon fiber	IM-600-6k (Toho Rayon)
Carbon fabric	Fabric; plain weave (0°/90°) W6E01 Areal weight; 200 g/m^2 Count warp and fill; 492 yarn/m
Stitched glass fiber	B150 1/4 10.4z x-2 (Unitica Ltd.)
Polymer	MSP type-L (STM-5L-A, Mitsui Chemicals) liquid type, $M_\mathrm{n} = 804$, $M_\mathrm{w} = 2124$
Fiber fraction	54–56 vol% ($x : y : z = 1 : 1 : 0.02$)
Ply	20 (Nominal thickness 4.5 mm)
Cure temperature	Pre-cure; 453 K, 4 h Post-cure; (a) 473 K, 2 h, (b) 673 K, 2 h
Fabricator	Japan Aircraft MFG Co., Ltd.

stitched with glass fibers (Unitica Co. Ltd., Japan). The polymer was heated at 368 K and impregnated into a stitched preform with pressure of 0.98 MPa. After polymer impregnation, it was heated at 453 K for 4 h. High quality composites were also obtained by an RTM processing. The composite laminates fabricated by the prepreg consolidation and RTM processing were post-cured at 473 K, 573 K, or 673 K for 2 h under nitrogen gas atmosphere.

2.4. Mechanical testing

Compressive tests were conducted with I-shaped lateral supports according to an end-loading test configuration similar to ASTM-D695-85. Nominal sample size was 25.4 mm in width, 105.5 mm in length, and 4 mm in thickness without tabs. A mechanical type testing machine (Model 8228, Instron, USA) was used for compressive tests under a constant displacement rate of 1.0 mm/min. For high temperature compressive testing, a specimen and a test fixture were held for 10 min after reaching the test temperature with heating rate of 3 °C/min. Elastic modulus was measured by using strain gauges affixed on both sides of specimen surface at room temperature.

3. RESULTS AND DISCUSSION

3.1. Cure kinetics and thermosetting reaction

Typical DSC results for MSP polymer (type-S) are plotted in Fig. 2, and estimated cure kinetic parameters are listed in Table 3 using Friedman's method [7]. Heat generation of type-L polymer was approximately twice as much as that of type-S.

Figure 3 shows FT-IR spectra for non-cured and cured MSP (type-S) polymer at 423, 473, 573 K for 2 h, respectively. An IR absorption peak around 3300 cm^{-1} $(-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{H})$ decreased with heat treatment temperature, which suggests that the

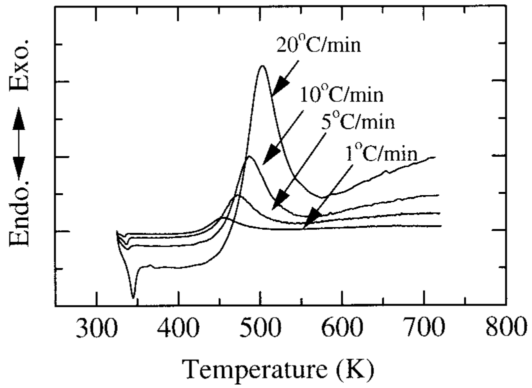


Figure 2. Differential scanning calorimetry (DSC) result of MSP polymer (type-S) in Argon atmosphere. Heating rate was 1, 5, 10, and 200 °C/min.

Table 3.
Cure kinetic parameters of MSP polymers (type-S and type-L)

(lot #)	MSP type-S (STM-3S)	MSP type-L (STM-5L-A)
A (1/s)	2.2×10^7	3.7×10^9
E (kJ/mole)	90	112
n	1.2	1.2
Q (J/g)	179	365

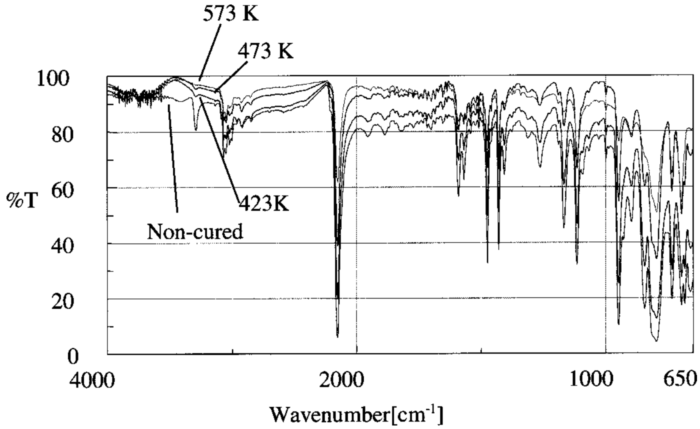


Figure 3. Fourier transform infrared (FT-IR) spectra of non-cured and cured MSP polymer (type-S). Cure temperature was 423, 473 and 573 K.

heat generation measured by DSC corresponds to the hydrosilylation reaction between Ph—Si—H and terminal —C≡C—H in MSP polymer. Any other obvious difference between non-cured and cured polymer at 473 K could not be observed in the FT-IR spectra. Heat generation due to the Diels–Alder reaction between —C≡C— and —C≡C— above 473 K could not be measured by DSC. However, an absorption peak around 2200 cm^{-1} decreases with heat treatment temperature, which suggests decreases in —Si—H bond due to the hydrosilylation reaction, and —C≡C— bond due to the Diels–Alder reaction.

3.2. Mechanical properties

Figure 4 shows compressive strength of the composites at room temperature, as a function of heat treatment temperature. The compressive strengths of the composites cured at 473 K did not compare well with typical graphite/epoxy composites [8]. Furthermore, strength degradation of the composites was considerable after heat treatment above 573 K, and the compressive strengths were quite poor. It should be noticed that the strength degradation due to heat treatment is irreversible. Stitched composite processed by an RTM has a little better strength than the non-stitched composites at high temperature. Young's modulus at room temperature was

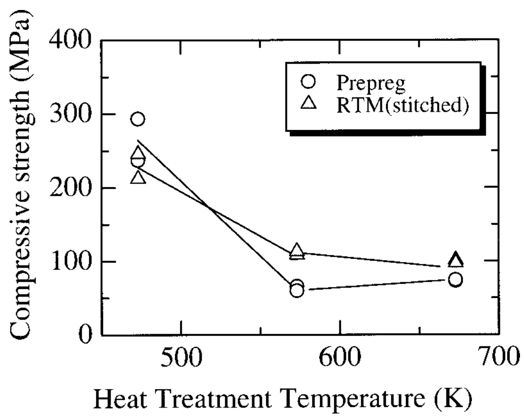


Figure 4. Compressive strengths of the composites at room temperature as a function of heat treatment temperature.

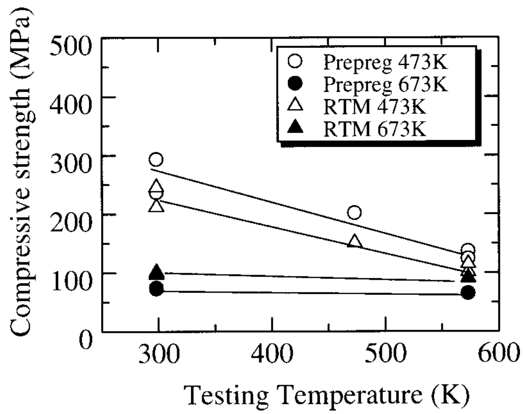


Figure 5. High temperature compressive strengths of the composites cured at 473 and 673 K.

61.8 GPa for the composite laminate processed by a prepreg consolidation method, and 71.7 GPa for the stitched composite laminate processed by an RTM method, which corresponds to the fiber volume fraction as shown in Table 1 and Table 2.

Compressive strength results at elevated temperature are plotted in Fig. 5. The compressive strengths of the composites cured at 473 K considerably decreased with temperature. Although the strengths of the composite cured at 673 K were almost constant up to 573 K, the strengths were quite poor. It can be observed that the compressive strength was a little bit improved by stitched fibers.

Figure 6 shows an SEM micrograph of the composite cross-section after heat treatment at 673 K. Many matrix cracks were observed in the transverse fiber bundles and resin rich regions. It is supposed that delaminations derived from these matrix cracks decreased the compressive strength of the composites. The result of thermo-mechanical analysis (TMA) of type-S polymer cured at 423 K is shown in Fig. 7. The volume of cured resin gradually shrunk during heat treatment

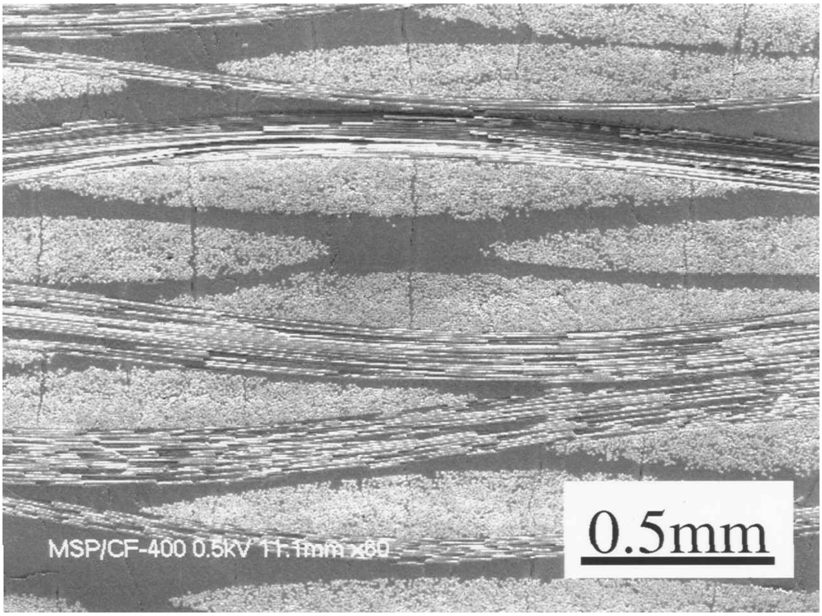


Figure 6. SEM photograph of the composite cross section after heat treatment at 673 K.

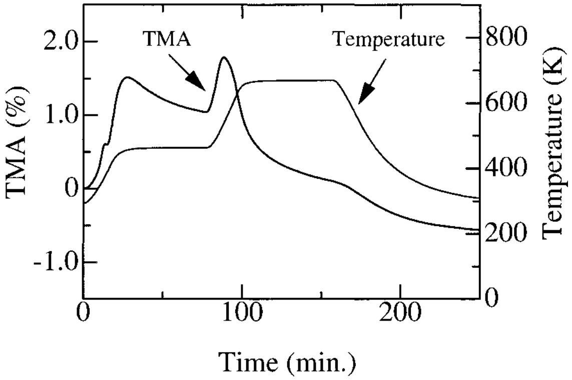


Figure 7. Thermal mechanical analysis (TMA) result of MSP polymer (type-S) cured at 423 K in Argon atmosphere.

at 473 K for 2 h, and large volume shrinkage is observed above 550 K. The shrinkage was caused by post-curing reaction due to the Diels–Alder reaction, and subsequent increase in the cross-link density. As a result, residual stress in matrix increased after cooling, and many matrix cracks were propagated in transverse fiber bundles. Furthermore, the polymer became brittle with cross-link density, and the embrittlement also influenced strength degradation of the composites.

To improve the mechanical properties of MSP polymer, the polymer blend technique with polyimides seems to be the effective method. Furthermore, basic polymer structure design for reducing the cross-linking density is also important to improve the toughness. Although stitched fibers in composite are certainly effective, it is impossible to improve the strength of MSP-CFRP sufficiently.

4. CONCLUSIONS

In this study, carbon fiber reinforced composites of which the matrix was silicon containing polymer MSP were made by a prepreg consolidation method of plain 2D woven prepreg sheets, and a resin transfer molding (RTM) method with a stitched plain 2D woven fabric. The processing conditions have been established for both prepreg consolidation and RTM method with polymer cure kinetics analysis. Compressive tests were conducted to evaluate mechanical properties of the composites. However the strength of the composites were poor at elevated temperature and after heat treatment above 473 K. This was attributed to embrittlement and shrinkage of the polymer during heat treatment above 473 K. Although MSP polymer has many attractive properties as matrix resin of high temperature polymer based composite, improvement of mechanical properties after heat treatment is indispensable for realistic engineering applications.

Acknowledgement

The authors thank Mr. S. Iwasawa and Mr. Y. Iwahori of Japan Aircraft MFG. Co. Ltd. for their assistance in development of an RTM processing.

REFERENCES

1. M. Itoh, M. Mitsuzuka, K. Iwata and K. Inoue, A novel synthesis and extremely high thermal stability of poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene], *Macromolecules* **27**, 7917–7919 (1994).
2. M. Itoh, K. Inoue, K. Iwata, M. Mitsuzuka and T. Kakigano, New highly heat-resistant polymers containing silicon: poly(silylene ethynylene phenylene ethynylene)s, *Macromolecules* **30**, 694–701 (1997).
3. M. Itoh, K. Inoue, K. Iwata, J. Ishikawa and Y. Takenaka, A heat-resistant silicon-based polymer, *Adv. Mater.* **9** (15), 1187–1190 (1997).
4. M. Narisawa, H. Takao, J. Hoshino, K. Okamura and M. Itoh, Formation of amorphous carbon containing silicon from a new organosilicon precursor, *J. Ceram. Soc. Japan* **104**, 812–815 (1997).
5. T. Ogasawara, T. Ishikawa, T. Yamada, R. Yokota, M. Itoh and S. Nogi, Thermal response and ablation characteristics of novel carbon ablator with silicon containing polymer for re-entry capsule, in: *Proc. 22nd ISTS (International Symposium on Space Technology and Science), 2000-c-35p* (2000).
6. D. Frank-Susich, D. Laanamen and D. Ruffner, Computer-aided cure optimization, in: *Proc. 37th Int. SAMPE Symposium*, pp. 1075–1088 (1992).
7. H. L. Friedman, Kinetics of thremal degradation of charforming plastics from thermogravimetry. Applications to a phenolic plastic, *J. Polym. Sci. (Chem.)* **6**, 183–195 (1965).
8. See, for example, *The Composite Materials Handbook-MIL 17: Materials Properties, Vol. 2*, pp. 4.1–4.220. Technomic Publishing Company, Inc., Lancaster, PA (1999).