Advanced Composite Materials
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tacm20

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To cite this article: L. M. Manocha , E. Yasuda , Y. Tanabe & S. Manocha (2000): Processing of carbon fiber reinforced silicon oxy-carbide matrix composites through the sol-gel route, Advanced Composite Materials, 9:4, 309-318

To link to this article: http://dx.doi.org/10.1163/15685510052000129

Adv. Composite Mater., Vol. 9, No. 4, pp. 309–318 (2000)

Processing of carbon fiber reinforced silicon oxy-carbide matrix composites through the sol-gel route

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Received 20 September 1999; accepted 30 July 2000

Abstract—Restricted applications of carbon–carbon composites due to their susceptibility to oxidation at high temperatures has renewed interest in all aspects relating to fiber reinforced glasses and ceramics. These include choice of reinforcing fibers and matrixes, their processing, fiber/matrix interactions as well as performance under varying conditions. Present studies have been performed to fabricate carbon fiber reinforced Silicon oxy-carbide matrix composites through sol-gel route using tetraethylorthosilicate (TEOS) and 1,4-butanediol as starting precursors. The composites have been fabricated by a polymeric composites route. The structural development specially at the fiber/matrix interface have been studied using SEM. On pyrolysis of the composites at 1000°C, the matrix has been found to be well surrounding the fibers; still, the composites exhibit mixed tensile cum shear mode failure under flexural loading. No oxidation of the fiber surface by oxygen present in silicon oxy-carbide is observed. The composites have been further heat treated to a temperature of around 1450°C. Though consolidation of the matrix is observed to be increased, the fibers are not damaged. XRD analysis of the matrix in the composites exhibit development of SiC. SEM examination of the composites' cross-section does not exhibit any strong reaction between fibers and matrix. Composites heat treated at 1450°C exhibit about 30% improvement in flexural strength over those processed at 1000°C, maintaining the non-catastrophic fracture.

Keywords: Sol-gel; carbon fiber composites; silicon oxy-carbide; fiber/matrix bonding; mechanical properties; composites fracture.

1. INTRODUCTION

A broad range of industrial sectors requiring high temperature operations have the potential for using fiber reinforced glass and ceramic matrix composites (FGCMC).

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Chemical processing, refining operations, power generation, and heat engines all can benefit from the use of FGCMC [1]. Poor oxidation resistance of carbon/carbon composites and the necessity to improve fracture toughness of conventional ceramics has accelerated interest in ceramic matrix composites. Thermally stable reinforcing fibers as well as the matrixes are the prime requirements for high performance ceramic matrix composites intended for reliable structural applications at high temperatures. Therefore, current research is concentrated on development and performance studies on small diameter ceramic fibers [2], glass and ceramic matrixes as well as on the fiber/matrix interactions [3] during high temperature processing and applications. All types of ceramics are being investigated as potential matrixes for fiber reinforced ceramic composites. Silicon- and carbon-based ceramics are getting more attention since with silicon there is wider choice of making ternary and multi-element glasses and ceramics with processing routes like CVD, polymer pyrolysis or sol-gel. Carbon incorporated silica in the form of silicon oxy-carbide having better thermal and mechanical properties than silica is a futuristic matrix material for low-cost glass and ceramic matrix composites. Carbon fibers as such, because of their reaction with oxygen at high temperatures, are not preferred as reinforcements with oxidic glasses. In silicon oxy-carbide glasses, the reactivity of oxygen may be reduced due to inherent presence of carbon. Silicon oxy-carbide glasses (black glasses) are produced through pre-ceramic polymers (siloxanes) or through sol-gel route [4].

Previous studies by the authors [5] showed that organic–inorganic hybrid gels can be prepared by hydrolysis-condensation reactions of tetraethylorthosilicate with 1,4-butanediol. The characterization of the gels by infrared spectroscopy showed the incorporation of carbonaceous groups in the polymeric structure and Si–C bonding in the glasses. Pyrolysis of the gels at 1000°C resulted in X-ray amorphous, hard black glasses similar to oxycarbide glasses obtained by pyrolysis of siloxanes. On further heat treatment to 1400–1600°C, development of cristobalite structure and crystalline silicon carbide was observed in the otherwise amorphous black mass.

In sol-gel processing, since the reactants are in liquid form and the viscosity of sol can be controlled until gellation, the processing routes for polymer matrix composites can be conveniently used for making fiber reinforced ceramic matrix composites with sol-gel derived matrix precursors. As compared to conventional melt infiltration technique, the processing temperatures used in this technique are lower and yet the composites can be used for high temperature applications. One can also investigate the fiber/matrix interactions at various stages of processing which is the controlling factor for fracture behaviour and mechanical properties of ceramic matrix composites. Silicon oxycarbide obtained through pyrolysis of organic–inorganic hybrid gel [5] was found to exhibit good resistance towards oxidation at 1000°C. This attracted the use of this matrix material for making fiber reinforced composites and their structural studies [6]. The present paper describes the processing of carbon fiber reinforced silicon oxy-carbide composites using the sol-gel route. The main emphasis of this study has been to investigate fiber/matrix interactions in these composites and their effect on the mechanical properties of the composites.

2. EXPERIMENTAL

Figure 1 shows the schematic of the technique used for fabrication of carbon fiber reinforced silicon oxy-carbide composites. This included prepreging of the reinforcements with siloxane gels, consolidation of prepregs and pyrolysis under inert atmosphere. Toray carbon fiber fabric 6381 made of T300 high strength carbon fiber tows, each tow consisting of 3000 monofilaments, was used as reinforcements. The weave pattern of carbon fabric was 8 harness satin. The matrix sol was synthesized by mixing tetraethyl orthosilicate (TEOS) and 1,4-butanediol in CCl_4 with molar ratios of TEOS : BD : CCl_4 as 1 : 4 : 2. 1,4-Butanediol cause hydrolysis of TEOS and also introduces carbon containing compounds in the molecular chain which on high temperature treatment results in silicon oxy-carbides. The detail studies on the matrix, hydrolysis, gellation and sintering to silicon oxycarbide is described elsewhere [5]. Prepregs were prepared by dipping carbon fabric in the viscous sol. Eight pieces of these prepregs were consolidated in a die under a slight pressure of about 3 KPa (press consolidation). These were then dried at 180°C during which the matrix transformed from viscous sol to gel and ultimately to solid polymeric composite. The polymeric composites were then pyrolysed to 1000°C under nitrogen at normal pressure. Some of the composites were further heat treated to 1450°C in argon since, around that temperature, resintering of the matrix takes place. The microstructure of the composites and fiber/matrix bonding were studied using Hitachi 3000N Scanning Electron Microscope (SEM). The flexural strength

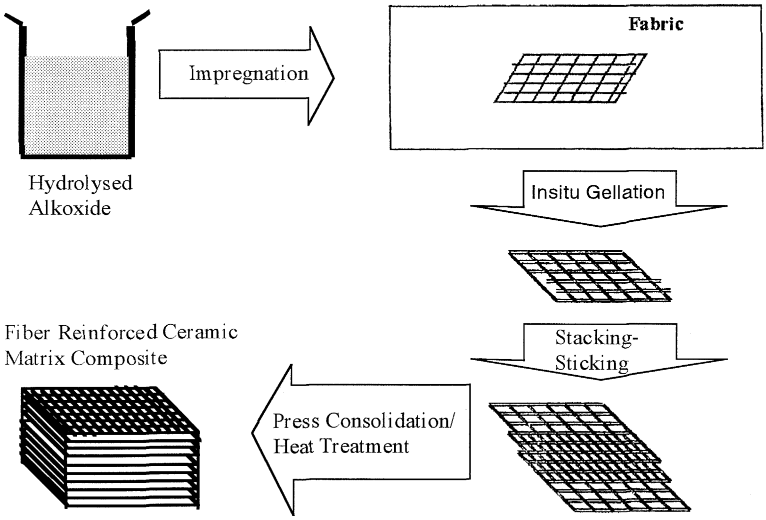

Figure 1. Processing of fiber reinforced ceramic matrix composites by the sol-gel route.

of the composites (150 mm long × 10 mm wide × 4 mm thick) was measured by three-point bending at span length of 80 mm maintaining span to depth ratio of 20 using Instron Universal Testing Machine 4483. In order to study the structure of the Si–O–C matrix with and without incorporation of fibers, the matrix in the heat-treated composites was separated from the fibers mechanically by careful slow grinding in a mortar and pestle, followed by sieving through a sieve of 400 mesh size. Though utmost care was taken that the matrix so separated does not contain carbon fibers, it might still contain about 8–10% fine powder of carbon fibers, ground along with the matrix. The structure of monolithic matrix (prepared without fibers) and the matrix from the composites (mechanically separated) were studied by FTIR using Shimadzu FTIR-8300 and by XRD using Regaku X-ray Diffractometer.

3. RESULTS AND DISCUSSION

3.1. Structure of the matrix with and without reinforcement

Polymers on carbonization are known to yield X-ray amorphous, isotropic, non-graphitizable carbons. However, in the case of carbon/carbon composites, the polymer-derived carbon matrix is found to change from isotropic to anisotropic due to stresses generated in the composites during pyrolysis [7]. These stresses are generated due to difference in shrinkage characteristics of carbon fibers and pyrolysing matrix as well as fiber/matrix bonding. The organic–inorganic hybrid gel derived Si–O–C matrix as such is also amorphous in nature. In order to study the effect of fiber reinforcement on the structure of matrix, the Si–O–C monolith as well as the Si–O–C matrix from the composites heat-treated to the same temperatures were analysed by FTIR and XRD. Figure 2 shows FTIR spectra of the two matrices having undergone the same heat treatment temperatures. The two matrices heat-treated to 1000°C exhibit identical FTIR spectra. These show prominent peaks at 800 cm^{-1} due to formation of a three-dimensional SiO_4 tetrahedron. A broad band at 1000–1250 cm^{-1} may presumably be due to simultaneous development of some overlapping peaks of Si–O–C at 1080 cm^{-1} and SiC at 1120 cm^{-1}. It shows that up to 1000°C heat treatment, the fibers do not influence the structure of the matrix. However, the FTIR spectra of the Si–O–C matrix from the composite heat-treated at 1450°C exhibit a shoulder around 820 cm^{-1} due to SiC. It suggests that at higher heat treatment temperatures (around 1450°C), the structure of the matrix is influenced by presence of the carbon fibers. Figure 3 shows the XRD patterns of the matrices. The XRD pattern of the matrices heat-treated at 1000°C are alike, typically of amorphous glasses except that the spectra of the matrix from the composites exhibit a peak at around $2\theta = 22.5°$, which may be due to a small amount of fine carbon fiber powder, having passed the sieve along with the matrix, overlapping with that of crystobalite. Since carbon fibers are of high strength type, these will not show the characteristic graphite peak around 26° but, rather, show a broad peak at lower angles. As seen from Fig. 3, there

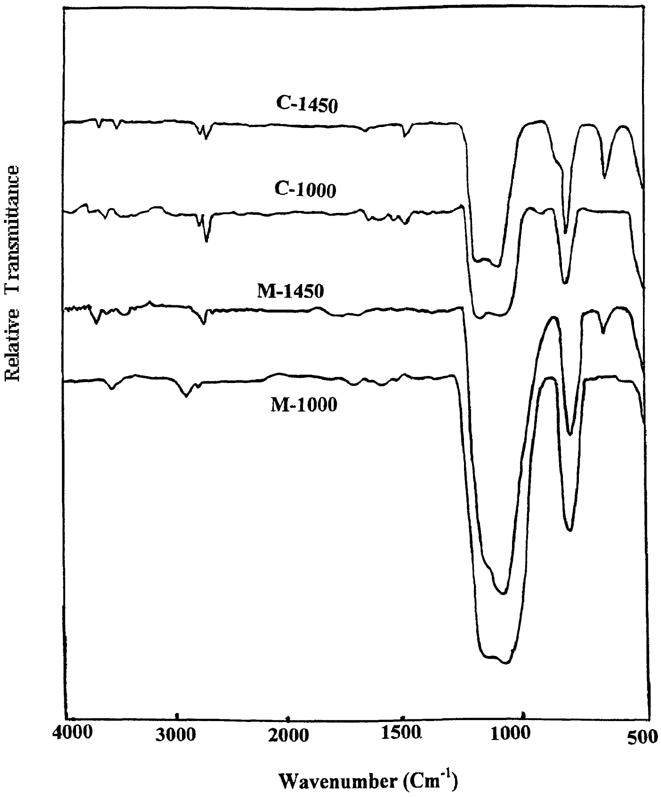

Figure 2. FTIR spectra of the Si-O-C matrices processed at different temperatures: (a) M-1000, monolith at 1000°C; (b) M-1450, monolith at 1450°C; (c) C-1000, matrix from composites processed at 1000°C; (d) C-1450, matrix from composites processed at 1450°C.

is a marked difference in the XRD spectra of the matrices heat treated to 1450°C. The monolith matrix exhibits a broad band with a peak around $2\theta = 22°$ due to a combination of amorphous Si–O–C, carbon, silica and due to crystobalite (like that of composite matrix at 1000°C), a small peak at $2\theta = 35.8°$ due to SiC. Formation of SiC may be due to reaction between free carbon and SiO_2 present in the Si–O–C matrix. However, in the matrix from the composites heat treated to l450°C, the peaks due to crystalline phases are much sharper, especially at $2\theta = 35.8°$ due to SiC. This supplements the findings from FTIR spectra that at 1450°C, the structure of the matrix is to a small extent influenced by the presence of carbon fibers. In composites, the matrix is more compacted. Therefore, the reaction amongst the constituents (SiO_2, amorphous carbon) within Si–O–C increases. At 1450°C some reaction could take place between carbon fiber surface and the Si–O–C matrix to result in formation of SiC. However, reaction between amorphous silica and amorphous carbon in the matrix is more probable than between amorphous silica and the ordered surface of carbon fibers. Therefore, the former reaction is expected to proceed at a higher rate than the latter.

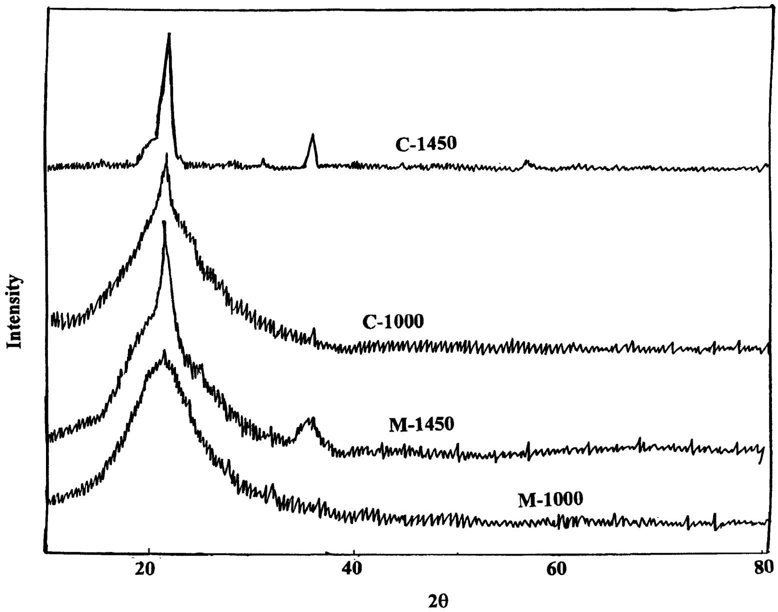

Figure 3. XRD spectra of the Si-O-C matrices processed at different temperatures: (a) M-1000, monolith at 1000°C; (b) M-1450, monolith at 1450°C; (c) C-1000, matrix from composites processed at 1000°C; (d) C-1450, matrix from composites processed at 1450°C.

Table 1.
Characteristics of carbon fiber reinforced silicon oxy-carbide matrix composites

	Heat treatment	Temperature
Properties	1000°C	1450°C
Fiber volume (%)	30	36
Density (kg/m^3)	1340	1520
Open porosity (%)	24	20
Flexural strength (MPa)	300	380

3.2. Microstructure of the composites

Though the matrix gel alone when pyrolysed to 1000°C is found to undergo a weight loss of 55% [5, 6], carbon fiber reinforced model composites with sol-gel derived siloxanes as matrix precursor exhibited good processibility and structural integrity. The physical characteristics of the composites at different stages of heat treatment are compiled in Table 1. The composites processed at even 1000°C possess good density. Figure 4 shows SEM micrographs of the fractured surface of the composites pyrolysed to 1000°C and 1450°C. The matrix is found to be well surrounding the fibers. The fibers in the composites heat treated to 1000° were found to have the same shape and cross-section as in the fiber strand thereby confirming that there

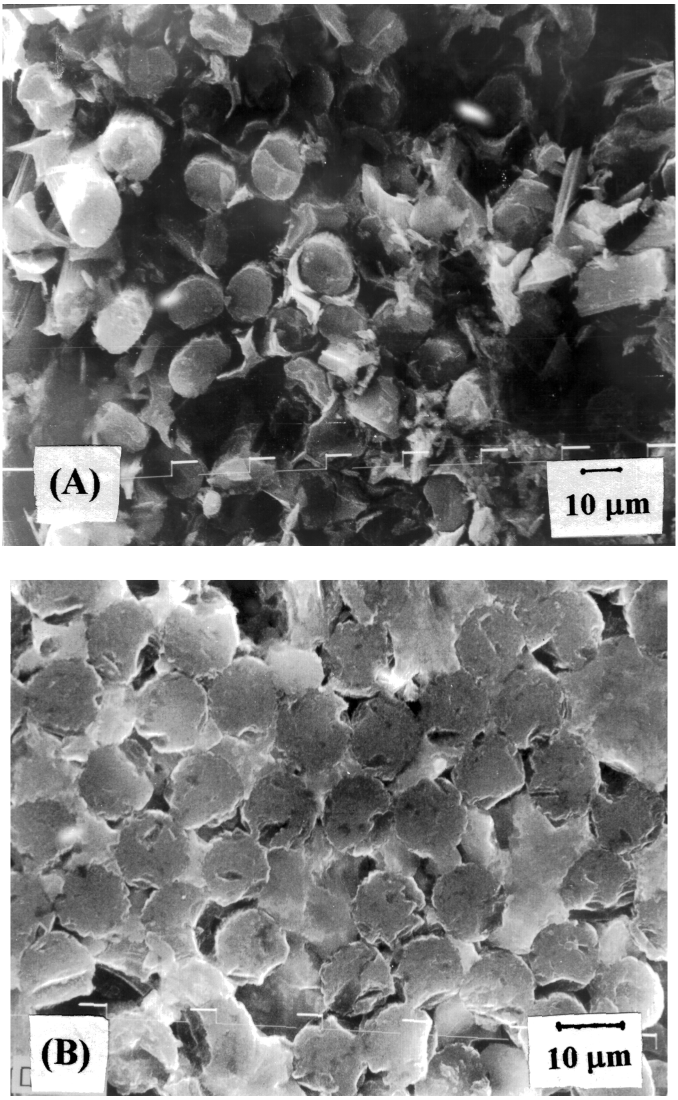

Figure 4. SEM micrographs of the cross-section of the composite processed at (A) 1000°C and (B) 1450°C.

was no oxidation of carbon fibers by the oxygen present in the matrix. However, gross porosity was observed in matrix-rich regions due to evolution of water and other reaction products during drying and pyrolysis. Most of the porosity was interconnected and hence could be filled in by reimpregnation of the composites with matrix sol followed by gellation, drying and pyrolysis.

Though a good fiber/matrix bonding was observed in polymer as well as in pyrolysed composites, no fiber damage was observed due to matrix pyrolysis shrinkage cracks or fiber/matrix chemical reactions. On heat treatment of the composites to 1450°C, sintering of the matrix takes place leading to shrinkage of the composites in the thickness direction by about 20%. This results in decrease of porosity and increase in density (Table l). In these heat-treated composites too, though the matrix is well compacted around the fibers, the shape of the fibers is found to remain unaltered. From SEM micrographs, it is found that no gross chemical reaction takes place between the fibers and Si–O–C matrix at 1450°C. If it occurs at all, it might be at the surface at nano scale.

3.3. Mechanical properties and fractographic studies on the composites

The flexural strength of the composites are included in Table 1. The composites processed at 1000°C exhibit fairly good strength. On heat treatment to 1450°C, the composites exhibit 30% increase in flexural strength which is attributed to compaction of the matrix and hence to low porosity of the composites.

Figure 5 shows load/displacement diagrams of the composites tested by three-point bending. Like a typical ceramic matrix composite, it exhibits a linear stress/strain behaviour followed by a kink due to onset of matrix cracking. Both the composites processed at 1000°C and at 1450°C exhibit non-catastrophic fracture. These correspond to the characteristic stress/strain behaviour of a fiber reinforced ceramic matrix composite having physical bonding between fibers and matrix. This type of bonding can also be inferred from SEM micrographs of the fractured faces of the composites shown in Fig. 6. The SEM micrograph of the composite processed at 1000°C (Fig. 6a) shows long clean fiber pullout without matrix attached to the fibers. This suggests that no chemical reaction is taking place between the carbon fibers and the silicon oxy-carbide matrix at 1000°C. The matrix is loosely packed within the fibers. On loading, the matrix contributes in distribution of the stresses amongst the fibers without contributing much towards bearing the stresses. Stresses are mainly borne by the fibers. On fracture, the matrix, which is already porous and

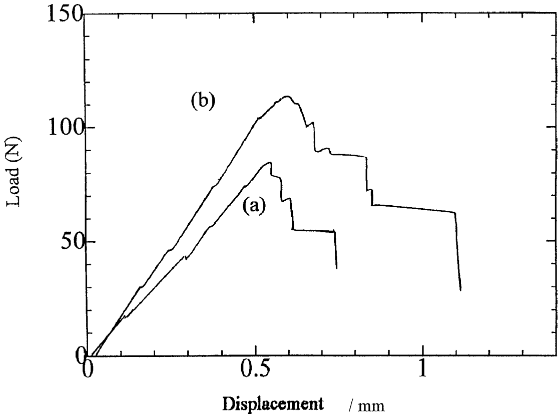

Figure 5. Load/displacement curves during bend testing of the composites processed at (a) 1000°C and (b) 1450°C.

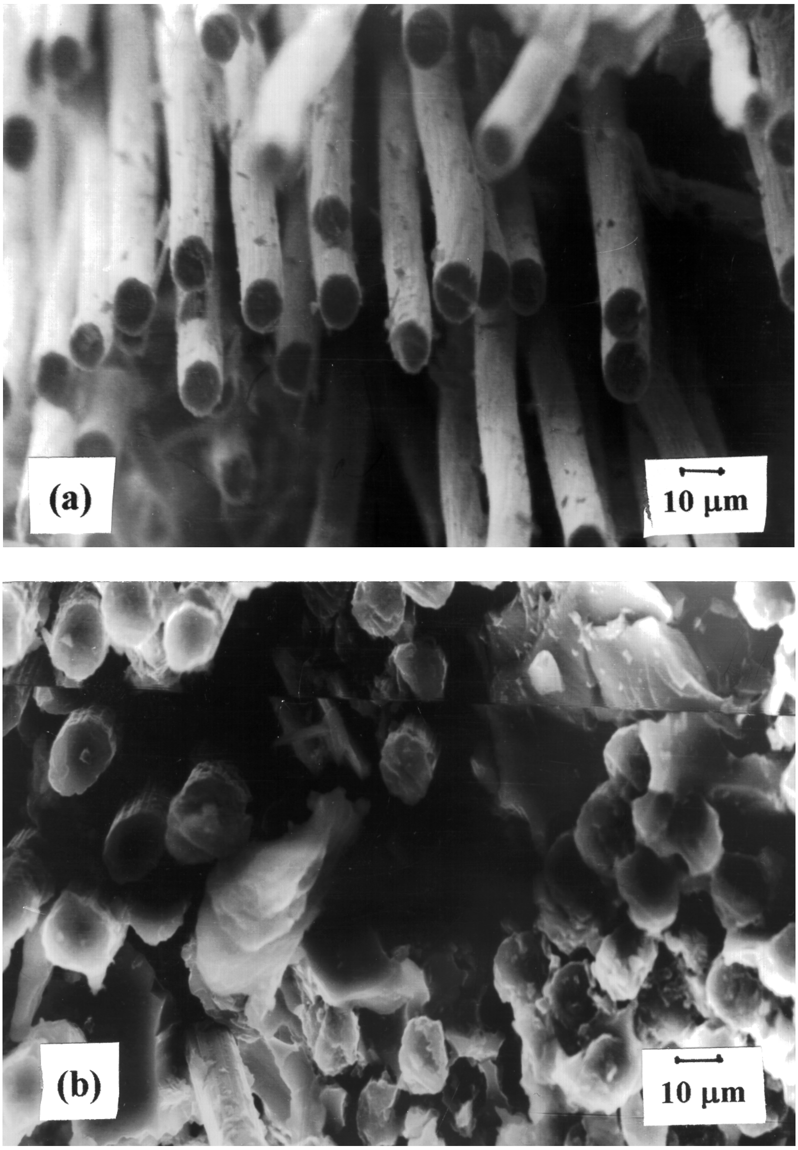

Figure 6. SEM micrographs of the fractured faces of the composites after bend testing, processed at (a) 1000°C and (b) 1450°C.

cracked, gets dusted away leaving the fibers naked. Even the composites processed at 1450°C exhibit fiber pullout type fracture (Fig. 6b). However, in this case, the fiber pullout length is smaller and the matrix can be seen within the fibers. This is because in these composites, the matrix has less voids and is well compacted in between the fibers. On loading, the matrix contributes towards bearing stresses as well as helps in distribution of the stresses amongst the fibers. On fracture, it does not dust out but retains integrity. However, no significant matrix is seen adhering to the pultruded fibers. This suggests that even at this stage of processing or heat treatment, there is no substantial chemical reaction between the fibers and the matrix. The fiber/matrix bonding is of purely physical type. The IR spectra and XRD analysis of the composites heat-treated at 1450°C show formation of SiC, but the fibers in the fractured composites are found to be more or less clean. This suggests that on high temperature heat treatment at 1450°C, the various constituents in the Si–O–C matrix have a greater probability of reaction within themselves than with the carbon fibers.

4. CONCLUSIONS

The organic–inorganic hybrid gels synthesized from TEOS and 1,4-butanediol can be used as matrix precursors for making carbon fiber reinforced oxy-carbide glass composites. In the composites processed by present technique, the reinforced fibers are not damaged due to shrinkage cracks of the matrix during pyrolysis or high temperature sintering. The matrix gets compacted during high temperature sintering resulting in dense composites. The elemental constituents of Si–O–C matrix react during high temperature sintering to yield silicon carbide. No chemical reaction takes place between carbon fibers and the sol during pyrolysis to 1000°C or with oxy-carbide glass during high temperature sintering. Composites so made exhibit good fiber/matrix bonding and non-catastrophic fracture under fiexural testing.

REFERENCES

1. M. H. Van de Voorde and M. R. Nedele, CMCs research in Europe and the future potential of CMCs in industry, *Ceram. Eng. Sci. Proc.* **17** (4), 3–5 (1996).
2. C. L. Segal and M. Burg, Global trend in the demand for advanced fibers, *39th Intern. SAMPE Symp.*, pp. 2337–2338 (1994).
3. R. Naslain, Fiber-matrix interphases and interfaces in ceramic matrix composites processed by CVI, *Composite Interfaces* **1** (3), 253–286 (1993).
4. G. D. Soraru, Silicon oxycarbide glasses from gels, *J. Sol-Gel Sci. Tech.* **2**, 843–848 (1994).
5. S. Manocha, D. Vashistha and L. M. Manocha, Thermal evolution of hybrid organic–inorganic gels derived from reaction of 1,4-butanediol with tetraethoxysilane, *J. Sol-Gel Sci. Tech.* **16**, 221–226 (1999).
6. S. Manocha, D. Vashistha and L. M. Manocha, Sol-gel processing of silicon-based matrixes for carbon fiber reinforced ceramic composites, *Key Engineering Materials* **164–165**, 81–84 (1999).
7. E. Fitzer and L. M. Manocha, in: *Carbon Reinforcements and Carbon/carbon Composite*, pp. 242–243. Springer-Verlag, Berlin (1998).