Strengthening of C/C Composites through Ceramer Matrix

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Abstract

The polymer-ceramic hybrid, known as 'ceramer', was synthesized by a sol-gel process by incorporating different amount of alkoxide as source of silicon in resorcinol-formaldehyde in presence of basic catalyst to get different percentage of silicon in ultimate carbonized composites. FTIR of the ceramer confirms that it is a network of Si-O-Si, Si-O-CH$_2$ and Si-OH type groups linked with benzene ring. Different amount of silicon in the ceramer exhibits varying temperature of thermal stability and lower coefficient of thermal expansion as compared to pure resorcinol-formaldehyde resin. The lower value of CTE in ceramer is due to existence of silica and resorcinol -formaldehyde in co-continuous phase. Unidirectional composites prepared with ceramer matrix and high-strength carbon fibers show lower value of flexural strength at polymer stage as compared to those prepared with resorcinol-formaldehyde resin. However, after heat treatment to 1450 °C, the ceramer matrix composites show large improvement in the mechanical properties, i.e. with 7% silicon in the ceramer, the flexural strength is enhanced by 100% and flexural modulus value by 40% as compared to that of pure resorcinol-formaldehyde resin matrix composites.

Keywords : Carbon Fibers, Ceramer, Carbon fiber ceramer matrix composites, Sol-gel technique, Mechanical properties

1. Introduction

Carbon-carbon composite is a unique class of material possessing specific thermo-mechanical properties which can be tailored to give large number of applications in aircraft, defense sector and hydrogen gas turbine blades etc., [1, 2]. These composites are generally prepared from high strength carbon fibers and phenolic resin or similar thermosetting resin as precursor for carbon matrix. High-strength PAN based carbon fibers make strong interactions with resin matrix at polymer stage because of its high active surface area and reactive functional groups as compared to high modulus carbon fibers [3]. During pyrolysis of these composites because of the significant shrinkage of polymer matrix, carbon fibers get damaged. As a consequence composite does not gives theoretically expected mechanical properties and thus fails to realize full potential strengthening effect of carbon fibers in the carbon-carbon composites [4]. In order to overcome above drawbacks of carbon-carbon composites, specially from high strength carbon fibers and phenolic resin matrix, it is essential to modify the interface either by coating the carbon fiber surface or by modifying the matrix by incorporation of thermally stable compound which may not only reduce the thermal shrinkage of the matrix but also the interactions and thermal contraction between fiber and the matrix. In an earlier study authors made an attempt to control the interaction between carbon fiber and polymeric matrix by employing silica and titania based interfacial coating on the carbon fibers and found that the flexural

strength of composites enhanced by a factor of two as compared to as produced carbon fiber composites [5, 6]. In the present study, the phenolic resin (resorcinol-formaldehyde) matrix has been modified by incorporating inorganic silica network derived from an alkoxide source, through a sol-gel process [7-9]. The hybrid material prepared from a mixture of resorcinol-formaldehyde (organic) and a ceramic i.e. silica (inorganic) is known as 'ceramer'. Such hybrid material (ceramer) should exhibit optimum combination of properties coming from the two components e.g. ductility and low density from the organic component and low thermal expansion, high temperature resistance, higher mechanical properties from inorganic components. Therefore, the present investigation was undertaken to understand the influence of silicon content in a ceramer on the mechanical properties of the carbon fiber reinforced ceramer matrix composites.

2. Experimental

The resorcinol-formaldehyde/silica hybrid known as ceramer was synthesized by a sol-gel process. The tetraethoxysilane (TEOS) was used as source of silica. The mixture of resorcinol formaldehyde and TEOS was taken in different molar ratios to obtain different percentage of silicon by weight in the ceramer matrix after carbonization to 1000 °C. Sodium carbonate was used as a basic catalyst. The formaldehyde solution used for synthesis of ceramer consists of formaldehyde (H-CHO); 37~41% weight/volume, methanol;

14% weight/volume and rest being water. Therefore, no additional solvent was required for hydrolysis and poly-condensation reactions. The ceramer samples prepared by incorporating different amount of alkoxides as silicon source were cured at 150°C and characterized for their structural analysis by FTIR. The coefficient of thermal expansion and thermal stability of cured ceramer was measured by Mettler Thermal Analysis system TA-4000.

Unidirectional polymer composites were prepared using PAN based T-300 carbon fibers (Tensile strength 3.5 GPa and tensile modulus 230 GPa, 6K tow) as reinforcement and pure resorcinol formaldehyde resin as well as ceramer as matrix precursor using wet winding and match mold die technique [5] keeping fiber volume fraction $50 \pm 2\%$. The polymer composites were heat treated at 1000 °C and 1450 °C respectively in inert atmosphere. The polymer and carbonized composites were characterized for mechanical properties on Instron universal testing machine model 4411 as per ASTM D-790-80. The ceramer prepared with the different amount of silicon and composites prepared there from were coded as follows:

C1, Resorcinol formaldehyde resin matrix composites;
C2, 7% Silicon from TEOS source ceramer composites;
C3, 15 % Silicon from TEOS source ceramer composites;
C4, 21% Silicon from TEOS source ceramer composites.
The percentage of silicon refers to carbonized samples.

3. Results and Discussion

3.1. FTIR Studies of Ceramer

Fig. 1 shows FTIR spectra of uncured and cured ceramer resins. In case of uncured ceramer (curve a), the absorption peaks at 466 and 790 cm^{-1} are due to the Si-O-Si asymmetric stretching vibration and symmetric bending vibration respectively [10, 11]. The strong peak at around 880 cm^{-1} is associated with Si-OH groups [12, 13]. The absorption peak
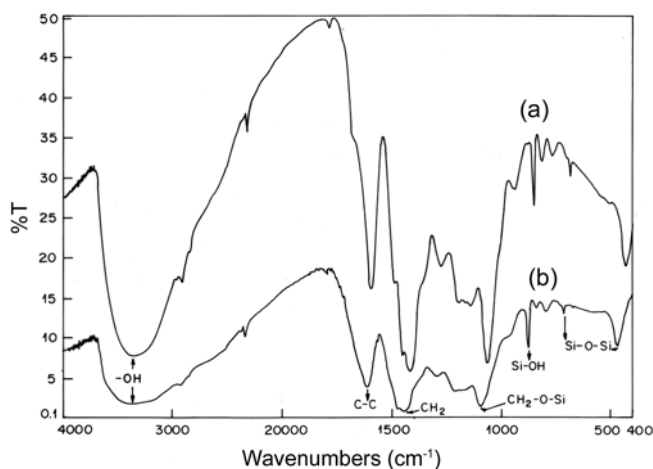
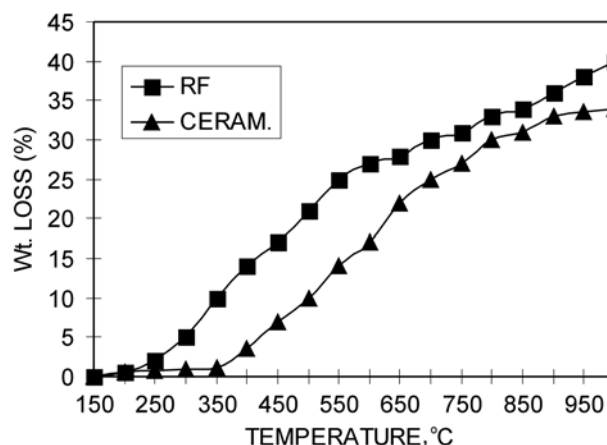**Fig. 1.** FTIR spectra of uncured and cured ceramer resins.

Fig. 2. The TGA curve of cured resorcinol-formaldehyde resin (RF) and ceramer (CERAM).

at 1091 cm^{-1} is associated with CH_2-O-Si network. Peak around 1200 cm^{-1} is of C-H stretching vibration of aromatic ortho-para substitution. The peak at 1441 cm^{-1} is associated with CH_2 stretching vibrations. The strong peak at 1614 cm^{-1} corresponds to C-C stretching mode of aromatic carbon. The broad absorption band at 3364 cm^{-1} is characteristic of OH stretching vibrations. It is observed from the FTIR results that functional groups present in the ceramer are polar in nature. In case of cured resin, the peaks corresponding to Si-OH, CH_2-O-Si and OH band, shifts towards higher wave numbers (curve b) due to poly-condensation reaction taking place at higher temperatures.

3.2. Thermo-mechanical analysis of ceramer

Fig. 2 shows the TGA curve of cured resorcinol form-aldehyde (RF) resin and the ceramer. The weight loss though steeper up to 600 °C for the resins, initiates at 200 °C for RF resin and 350 °C for ceramer. The overall weight loss is 40% for RF resin whereas it is only 33% for ceramer. This is due to formation of silicate network in the ceramer and removal of water trapped in silicate network as a result of evolution of reaction products at higher temperatures [7]. This makes the resin thermally more stable. Beyond 750 °C, the rate of weight loss slows down. It is interesting to note that the weight loss in ceramer gets restricted to ~10% (up to 600 °C) only as compared to 25% observed in case of RF

Table 1. TG analysis results of resins

Ceramer Code	Wt. loss start Temperature °C	% Weight Loss at 1000 °C
C1	200	40
C2	300	36
C3	250	34
C4	250	32

Table 2. Chemical analysis of ceramer

Ceramer Code	Actual % of Si in ceramer after 1000 °C
C1	00
C2	7.0
C3	14.5
C4	21.00
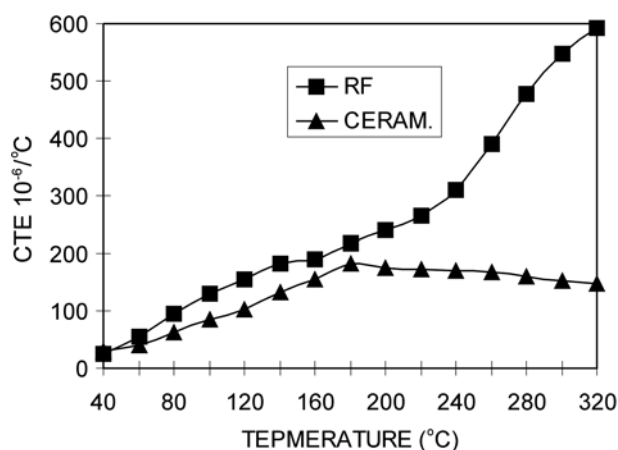
Fig. 3. The relative variation in coefficient of thermal expansion of cured (RF) resorcinol-formaldehyde resin and ceramer (CERAM).

resin. The TG curve also suggests that the ceramer resin is thermally stable up to about 350 °C and gives higher yield than RF resin. The TG results of all the ceramer samples are compared in Table 1.

Table 2 gives the total amount of Si present in ceramer matrices synthesized by using different concentration of TEOS. The silicon percentage was obtained from the residue of the cured ceramer heated in air at 1000 °C.

Fig. 3 shows the relative variation in coefficient of thermal expansion (CTE) as a function of temperature for cured C1 and C3 matrix. The curves indicate that two matrices behave quite differently. With increasing temperature, CTE of C1 increases moderately up to 150 °C and thereafter it increases sharply up to 350 °C. However, in case of ceramer, the CTE increases moderately up to 180 °C and then flatten up. The contrasting behavior has been attributed to orientation of the resorcinol formaldehyde chains between the silica domains, which is expected to occur only if the silica and resorcinol-formaldehyde component exist in co-continues phases [14]. The lower value of CTE in ceramer is further attributed to overall reduction in free volume by formation of a rigid network in the ceramer or tight silica network relative to resorcinol-formaldehyde components [7]. The lower value of CTE in case of ceramer should be conducive for reducing shrinkage occurring during pyrolysis. This should help therefore in improving mechanical properties of resulting com-
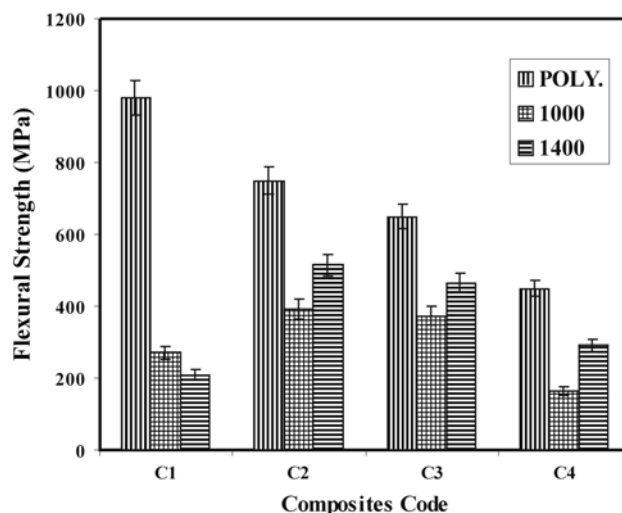
Fig. 4. Flexural strength of composites at different stages of processing.

posites.

3.3. Mechanical Properties of the Composites

Fig. 4 shows flexural strength of composites (C1-C4) at different stages of processing i.e. polymer stage at 150 °C, carbonized 1000 °C and HTT at 1400 °C. At polymer stage the value of flexural strength is higher in case of composites C1 as compared to ceramer (C2-C4) matrix composites, which could be attributed to stronger fiber-matrix interactions resulting in high stress transfer capability [3]. In case of the ceramer matrix composites (C2-C4), the presence of silica in ceramer matrix weakens the fiber-matrix interactions [15] resulting decreases in strength. However, upon carbonization (at 1000 °C) the trend is reversed, flexural strength of composite C1 decreases from 980 MPa to 270 MPa while same trend for composites C2 and C3. Ultimate value of flexural strength ~400 MPa for both C2 and C3 composites is higher than C1 composite. But on the other hand, strength significantly decreases in case of C4 composites. In case of composite C1 as explained earlier [16, 17], the shrinkage stresses developed during carbonization lead to matrix micro-cracking which upon the application of external stresses, even at small stress levels, allow cracks to propagate through fibers without any deviation at the

Table 3. Bulk density of composites at different temperatures

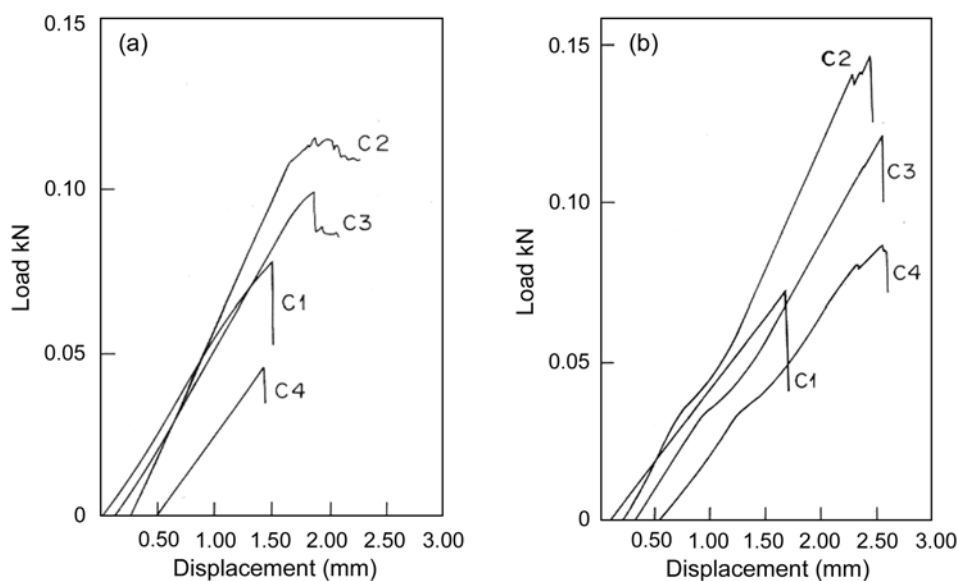| Composites Code	Bulk Density (g/cm³)	
	HTT 1000 °C	HTT 1450 °C
C1	1.31	1.33
C2	1.39	1.36
C3	1.32	1.30
C4	1.29	1.25

Fig. 5. Load-displacement curves of composites heat treated at (a) 1000 °C and (b) 1450 °C.

interface. As a consequence, poor mechanical properties of resorcinol formaldehyde resin derived matrix composites. In case of ceramer matrix composites the matrix microcraking is controlled by the lower degree of shrinkage of the matrix during carbonization and the formation of three dimensional silica networks around the carbon fibers. However, with increase in the amount of silicon, the flexural strength of composites C4 does not improve primarily due to the porosity generated in the matrix. As a result increases in stress concentration centre is responsible for degradation of the strength.

On further heat treatment of the samples to 1450 °C, the strong fiber matrix bonds are formed via formation of Si-O-C and Si-C linkages. Consequently significant improvement in flexural strength is observed in all the ceramer matrix based composites (C2-C4). On the contrary, the flexural strength of composite C1 decreases further because of the cracks developed during carbonization of the matrix may get enlarged by further heat treatment which ultimately dominates the flexural strength of the composites. The larger improvement in the value of flexural strength in case of composites C2 and C3 may also be attributed to the intrinsic characteristic of ceramer matrix i.e. better ductility and mechanical properties, and lower value of porosity (higher bulk density, Table 3). This is evident from Figure 5, showing load -displacement behavior of the composites C2 and C3. These composites fracture at a strain level which is much higher than that of composite C1. The flexural strength of composite C4 is lower than that of C2 and C3 mainly because of the presence of comparatively higher porosity as evident from their bulk density values (Table 3).

Variations in flexural modulus of composites are shown in Figure 6. At polymer stage, the contribution of matrix to
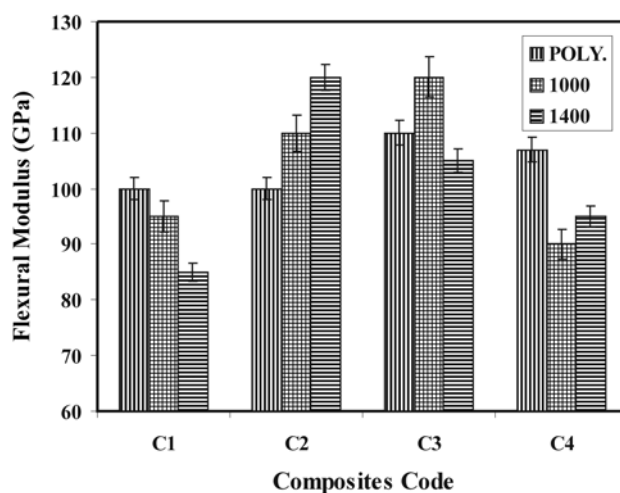

Fig. 6. Flexural modulus of composites at different stages of processing.

flexural modulus of the composites is negligible because the fiber modulus is always much higher than the matrix modulus. Therefore, in all the composites flexural modulus ranges between 95 GPa for composite C1 to 110 GPa for ceramer based composites. Upon carbonization to 1000 °C, flexural modulus of composite C1 decreases slightly while for ceramer matrix composite it registers significant increase. The value further increases to 120 GPa after HTT to 1450 °C for composite C2. The decrease in the flexural modulus in case of C1 composites is due to the large difference in strain to failure of carbon fiber and carbonized matrix, as a result the carbon fiber modulus is not fully exploited in these composites. The increases in flexural modulus in case of ceramer matrix composite C2 is due to

Table 4. Matrix failure displacement in 1450 °C heat treated composites

Composites Code	Matrix failure displacement (mm)
C1	1.7*
C2	0.5
C3	0.65
C4	0.78

*Displacement of composite.

the intrinsic characteristics of ceramer. It may be due to the fact that strain to failure of ceramer is higher as compared pure carbon derived from phenolic resin and becomes comparable to that of carbon fibers. It is therefore, possible to realize the carbon fiber modulus to a much higher extent in these composites. However, same as flexural strength of composites C4 shows lower value of flexural modulus after HTT at 1450 °C. The lower value of flexural modulus in C4 composite can be attributed to the different matrix texture and fiber-matrix interactions due to higher percentage of silicon.

Fig. 5 shows the load -displacement curve of the composite heat treated at 1000 °C and 1450 °C respectively. The composite C1 fracture is in pure tensile mode in both the cases (Fig. 5a and b). While ceramer matrix based composite heat treated at 1000 °C fracture in pure tensile mode but on heat treatment to 1450°C, shows mix mode of failure with initial microcracking in all composites i.e. nonlinear load -displacement curve (Fig. 5b). After the matrix microcraking in composites, there is further transfer of load till the maxima is reached. With increasing the silicon concentration in ceramer, the matrix failure (microcraking) load is nearly same but displacement is different which is shown in Table 4. As shown in the table, it noticed that in composite C2, matrix failure displacement is 0.5 mm, which increases with increasing the concentration of silicon and maximum value is 0.78 mm for composite C4. However, with increasing silicon concentration in ceramer matrix composites, porosity and voids also increase which inhibits further increase in the properties, rather it results into lower value of mechanical properties in composites C3 and C4.

4. Comclusion

A ceramer matrix, synthesized through a sol-gel process from a mixture of resorcinol- formaldehyde and different alkoxide source of silica, showed that ceramer is a network of Si-O-Si, Si-O-CH$_2$ and Si-OH type groups linked with benzene ring. The ceramer possessing different amount of silicon were found to be thermally stable up to 300~350 °C. The ceramer matrix exhibits lower thermal expansion as compared to pure RF resin due to the presence of silica and resorcinol formaldehyde in co-continues phase. The com-

posites prepared from ceramer matrix shows lower values of mechanical properties at polymer stage due to weak fiber-matrix interactions as compared to RF resin matrix composites. However, after heat treatment to 1450 °C, significant improvement in the mechanical properties of ceramer matrix composites was observed. From the results it is also observed that, an optimum amount of silicon in ceramer matrix is required to enhance the mechanical properties of composites. Higher percentage of silicon incorporated during the synthesis of ceramer matrix gives high porosity, which results in poor mechanical properties of the composites. There seems to be further scope of improving the properties of these composites by controlling the voids and porosity generated due to evolution of reaction products in sol-gel derived ceramer.

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