Improvement of Inter-face Layer Coating by Plasma Treatment of Carbon Fiber for Carbon Fiber Reinforced Silicon Carbide Composite Applications

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Abstract. Carbon fiber (CF) reinforced SiC (CF/SiC) composites are sought for high temperature application in areas of automobiles, aerospace and nuclear reactors due to their outstanding properties. However, CF/SiC composites have low durability owing to oxidation of CF upon air-exposure during high temperature applications. The inter-phase layer between fiber and SiC matrix is used in order to protect fiber from oxidation. Here, we have aimed to study the effect of air RF (13.56 MHz) plasma treatment on CF tow for improvement of SiO₂ inter-face layer coating by dip coating technique. The air RF (13.56 MHz) plasma treatments on CF tows and graphite proxy substrates (for 20, 40 and 60 min) have been analyzed by Scanning Electron Microscopy (SEM) and contact angle measurement, respectively confirmed the enhancement of wettability. Such plasma treated CF tows have been further used for deposition of SiO₂ coating and uniform deposition has been achieved for 20 min plasma treated CF as evident from SEM surface analysis. Whereas, Energy Dispersive X-ray Analysis (EDXA) and Fourier Transform Infra-Red spectroscopy (FTIR) measurements have been used to get elemental and bonding information of coated silicon substrates confirmed the high quality of SiO₂ coating. While tensile strength measurement verified the enhancement of tensile strength for plasma treated SiO₂ coated CF tows as compare to untreated CF tow, and optimum strength (1449 MPa) has been obtained for 20 min plasma treated SiO₂ coated CF tow with uniform coating properties. Hence, 20 min plasma treatment on CF tow is confirmed the beneficial effect on SiO₂ inter-face layer coating for CF/SiC Composites Applications.

1. Introduction

Carbon fibers (CFs) are widely used as reinforcements in composite materials due to their excellent properties such as low coefficient of thermal expansion, high modulus and strength, low density, good electrical conductivity and relative high flexibility [1-2]. In particular, CF/SiC (in which SiC act as a matrix) is well known for its high strength and stiffness as well as its low density, which makes it an attractive candidate for the aerospace, automobile industries, gas turbine engine and nuclear reactors applications [3-4]. However, continuous use of CF reinforced composite in oxidising environment is imposed temperature limit to lower than 500° C for high temperature applications. Such drawback could be overcome by protecting CF by an oxidative protection coating when they are exposed to oxidative and chemically aggressive environments. There are numerous research work reported for the
oxidative protective coating layer on CF such as carbides, nitrides and oxides by various coating techniques [5-6]. Among them, SiO2 based inter-face layer is one of the potential candidate which improves the oxidation resistance property of the CF tow and thus act as protective layer coating. SiO2 has also high melting point and an exceptional oxygen barrier property.

At same time, CF surface is also chemically inert in nature and has lower wettability, which leads to the most potential problem of inadequate adhesion of coating and hence weaker bonding between the fiber and coating. Poor adhesion and lower bonding strength of coating with fiber are resulted in insufficient oxidation protection of CF. Therefore, the surface treatment of CF is necessary, which increase the surface active sites as well as surface roughness for improvement of bonding strength between the fiber and coating. Various methods have been used for surface modification of CF, such as acid treatment, plasma treatment, rare-earth treatment and gamma irradiation [7]. Among those, plasma treatment is widely used to modify fiber surface chemically and structurally without much influencing their bulk mechanical properties.

In the present work, we have studied the effect of plasma treatment on CF tow for improvement of SiO2 inter-face layer coating carried-out by dip coating technique. We have attempted surface modification of CF by air plasma using RF (13.56 MHz) source for 20, 40 and 60 min prior to SiO2 deposition. The SiO2 coating on untreated and plasma treated CF tows are achieved by a dip coating technique with fixed 3 Nos. dipping cycles of coating to evaluate the surface modification effects. Surface morphology of plasma treated and SiO2 coated CF tows are investigated by SEM analysis. The contact measurement of untreated and plasma treated proxy graphite samples are carried out using optical contact angle goniometer, while chemical composition and bonding information of SiO2 coating on silicon substrate are obtained by EDXA and FTIR measurement, respectively. The tensile strength testing of the plasma treated coated and uncoated CF tows are also investigated in order to see the improvement of quality SiO2 coating as inter-face layer for CF/SiC composites.

2. Experimental

2.1. Materials
The CF tow used in this study is Poly-Acrylo-Nitrile (PAN) based “TAIRYFIL TC – 33 (6K)” CF tow purchased from Formosa Plastics Corporation (Taiwan). Tetraethyl Orthosilicate (TEOS, 98%) [Si (OC2H5)4] is used as SiO2 coating precursor obtained from Acros Organics (USA). Propan-2-ol (99.99%) for solvent and Hydrochloric Acid (HCl) for catalyst purpose are purchased from Rankem Chemicals (India).

![Figure 1. Process flow charts for (a) SiO2 coating solution preparation for dip coating of CF tow and (b) Dip coating processing steps for SiO2 coating on CF tow.](image)

2.2. Coating Solution Preparation
The SiO2 solution is prepared by the hydrolysis-condensation (sol-gel process) of SiO2 containing inorganic-organic compounds in which TEOS is used as the SiO2 precursor. In a beaker, known quantity of TEOS is added with propan-2-ol and the solution is continuously stirred for uniform mixing. In another beaker, HCl is added in known volume of water such that pH of the solution is kept
below 2 pH. This prepared pH solution is added drop wise into the mixture of TEOS and propan-2-ol while stirring. The final prepared solution is kept stirred for 3 hours at room temperature with fixed molar ratio of TEOS: Propan-2-ol: Water as 1: 4: 8. The whole process of preparation of SiO$_2$ coating solution is shown schematically by the flow chart in Fig. 1 (a).

2.3. Plasma Surface Treatment of CF
Prior to plasma treatment, all CF tows are de-sized using acetone for removal of any surface contamination as well as sizing layer. Then after, all de-sized CF tows are plasma treated in air RF (13.56 MHz) plasma formed between capacitively coupled disc electrodes (size = 22 cm dia) in a high vacuum system. All de-sized CF tows are treated for 20, 40 and 60 min time duration at pressure $5 \times 10^{-1}$ mbar and 25 watts coupled power. Looking to difficulty in contact angle measurement and hence wettability properties, high density graphite discs (Size = 10 mm dia) are used as proxies of CF tows to get relative trends of plasma treatment effect.

2.4. SiO$_2$ Coating on CF
Dip Coating unit (Model No. Ho-TH 02B) with infrared heater is used for SiO$_2$ coating, which is supplied by the Holmarc Opto-Mechtronic Pvt. Ltd (India). SiO$_2$ coating on all CF tows (de-sized, 20, 40 and 60 min plasma treated) are applied using dip coating technique with fixed process parameter such as 3 Nos. dipping cycles, 8 mm/sec withdrawal speed and 5 min dipping time. After each coating cycle, CF tow is dried at 150° C by infrared heater attached to the dip coating unit, followed by final heat treatments at 400° C for 60 min. The entire process steps of the SiO$_2$ coating on the fiber tow are represented by the flow chart in Fig. 1(b).

2.5. SiO$_2$ Coating Characterization
The surface morphology and chemical composition for plasma treated and SiO$_2$ coated CF tow are analysed using SEM and EDXA attachment (440i, LEO, UK), respectively. The wettability of graphite proxy substrates before and after plasma treatments are estimated by means of contact angle measurements, which are carried out using optical contact angle goniometer (OCA15, Dataphysics, Germany) as per the sessile drop method. The detail bonding information for SiO$_2$ coatings on silicon substrates are obtained by FTIR (Nicolet 6700, Thermo Electron Corp., USA) measurement. The Instron Universal Testing System (Model 5982) is used to measure tensile strength of all CF tows.

3. Results and Discussion

3.1. Effect of Plasma Surface Treatment on CF

![Figure 2. Contact angle measurements of plasma treated graphite samples. Inset images show for (a) untreated (b) 20 min and (c) 60 min plasma treated graphite samples.](image)

![Figure 3. SEM images of CF for (a) untreated, (b) 20 min, (c) 40 min and (d) 60 min plasma treated (Arrow marks show pitting effect on CF surfaces).](image)
Plasma is defined as an electrically conducting medium generally consisting of electrons, charged ions, and neutral atoms or molecules or both. Plasma treatment may not only enhance surface roughness (due to ion-bombardment) but also alter surface functional groups of treated CF. The effect of Air RF (13.56 MHz) plasma treatment on wettability by measuring contact angle for varying treatment time 20, 40 and 60 min on graphite proxy substrates are showed in Fig 2. The measured contact angle is drastically reduced from 117.6° (untreated) to 25.9° (20 min treated) and further reduced to 11.2° (60 min treated) confirmed the improvement of wettability (Fig 2 (a), (b) and (c)) for graphite proxy substrates and hence similar effect is assumed for CF tows. The detail SEM surface morphology analysis is revealed the clear micro-pitting effect for plasma treated surface of CF with increasing in nature for higher and higher treatment time duration (Fig. 3 (b), (c) and (d)) as compare to untreated CF (Fig. 3 (a)). The surface roughness increment increases the surface area which is major contributor to improvement of wettability and hence enhancement of mechanical interlocking between fiber and coating. Further, it is also noted that with increase in treatment time the enhancement of pitting structure are observed for 40 & 60 min plasma treated CF (Fig. 3 (c) & (d)).

3.2. SiO$_2$ coating Effect on CF
All CF tows (untreated and plasma treated) are coated by dip coating technique with fixed 3 Nos. of dipping cycles, 8 mm/s withdrawal speed, and 5 min dipping time in order to check plasma treatments effect on coating quality. SEM images are analysed in order to study the surface morphology of the SiO$_2$ coating on these CF tows (Fig 4 (a), (b) and (c)). SEM surface analysis is revealed that the uniformity and continuous coating is observed for 20 min (Fig. 4 (b)) in comparison to untreated CF tow (Fig 4 (a)). It is assumed that active species in the plasma aggressively attack the edges of tissue like structure of CF and creates micro-pitting region, essentially responsible for improvement of wettability and hence uniformity of coating. Whereas, deterioration of coatings for 40 min (SEM image not shown) and 60 min (Fig. 4 (c)) plasma treated CF tows are observed due to excessive coating because of intense plasma treatment effect as evident from SEM analysis (Fig. 3 (c) & (d)). The thickness values of coating on plasma treated CF are estimated in range of 2.74 to 3.02 μm by cross-section SEM analysis. Here, these values are obtained from plasma treated silicon substrates, which are coated with identical deposition parameters and such typical SEM cross-section measurement image is shown in Fig. 4 (d). At same time, chemical composition analysis by EDXA is clearly identified major Silicon and Oxygen elements peaks with well-defined stoichiometry in EDXA spectra (Fig. 4 (e)) and also atomic concentration analysis confirmed the SiO$_2$ coating. Whereas, FTIR measurement on coated silicon substrate is showed the presence of characteristic Si-O rocking bond peak at 453 cm$^{-1}$ apart from Si-O-Si asymmetric (1090 cm$^{-1}$) and Si-O bending (812 cm$^{-1}$) peaks confirmed the SiO$_2$ coating by dip coating process Fig. 5 (a).

Figure 4. SEM micrograph of SiO$_2$ coated CF tow for (a) untreated (b) 20 min treated and (c) 60 min treated. Whereas, (d) typical SEM cross-section image of SiO$_2$ coated silicon substrate and (e) EDXA spectra with inset table for obtained atomic concentration values.
The mechanical property of SiO₂ coated and un-coated CF tows are measured using Instron Universal Testing System. A total of five CF tows of each set of SiO₂ coated and un-coated CF tows are measured as per ASTM standard for better accuracy (Fig 5 (b)). The tensile strength of uncoated CF tow is 1036 MPa, while tensile strength of plasma treated for 20 min, 40 min and 60 min with SiO₂ coated CF tows are 1449, 1582 and 1294 MPa, respectively. It is observed that there is continuous increase in tensile strength with increase in plasma treatment time up to 40 min, which is due to improvement of SiO₂ coating. However, for 60 min, the tensile strength decreases due to the deterioration of coating as evident from the CF tow SEM image, as shown in Fig. 4 (c). So, the optimum tensile strength with uniform SiO₂ coating has been obtained for 20 min plasma treated SiO₂ coated CF tow with fixed 3 Nos. dipping cycles, withdrawal speed 8 mm/sec and dipping time 5 min.

4. Conclusion
Plasma treatment of CF tow for improvement of SiO₂ inter-face layer coating has been successfully attempted for composite application. The effect of plasma treatment on CF has been studied by SEM and contact angle measured on graphite substrates have confirmed the enhancement of wettability. Plasma treated CF tows have been further effectively used for deposition of SiO₂ coating and uniform deposition has been achieved for 20 min plasma treated CF tow as evident from SEM surface analysis. EDXA and FTIR measurements have been used to get elemental and bonding information of coated silicon substrates confirmed the high quality of SiO₂ coating. While tensile strength measurement verified the enhancement of tensile strength for plasma treated CF as compare to untreated CF tow, and optimum strength (1449 MPa) has been obtained for 20 min treated SiO₂ coated CF tow with uniform coating properties.

![Figure 5. (a) FTIR spectra taken for SiO₂ coated silicon substrate along with bare silicon substrate. (b) Tensile measurement of untreated and plasma treated SiO₂ coated CF tows.](image)

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