



# Graphene oxide grafted carbon fiber reinforced siliconborocarbonitride ceramics with enhanced thermal stability



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## ABSTRACT

Hierarchical structure consisting of graphene oxide (GO) grafted onto carbon fiber (CF) has been synthesized to improve the interfacial properties between the CFs and polymer matrix. The modified CFs are coated with siliconborocarbonitride (SiBCN) preceramic polymer by in situ polymerization to enhance their antioxidant and ablation properties. X-ray photoelectron spectroscopy were used to monitor the composition of the composites. Scanning electron microscopy images revealed that GO was successfully grafted onto CF (CF-g-GO) and coated with SiBCN preceramic polymer (CF-g-GO/SiBCN). Loading of SiBCN preceramic polymer on the surface of CF-g-GO increased remarkably compared to that on the surface of untreated CFs. Pyrolysis of CF-g-GO/SiBCN preceramic polymer at 1400 °C in inert atmosphere led to the formation of SiBCN ceramics with the approximate elemental composition of Si<sub>3</sub>N<sub>4</sub>/SiC/BN. TG results show that the thermal stability of the CF with ceramic layer has improved noticeably at high temperature.

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## 1. Introduction

Carbon-fiber reinforced polymer (CFRP) composites have attracted continuous attention over the past half century because they offer excellent mechanical properties, high strength-to weight-ratio, high rigidity, and chemical resistance. They exhibit potential applications in aerospace, automotive and civil engineering, and numerous industrial fields [1–3]. Besides, CFRP also possesses good in-plane tensile properties attributed to its equivalent weight in comparison to the traditional metallic materials. However, the performance of CFRP is often limited due to the existence of a weak interface between the fiber and surrounding polymer matrix [4]. This is ascribed to the smooth and inert surface of CF. Therefore, the interface between the CFs and matrix remains an important area of study and it plays a major role in determining the macroscopic shear, transverse, and out of plane properties of a composite [5].

Numerous techniques have been developed to improve the interfacial properties by modifying CFs using micrometer and nanometer scale materials such as carbon nanotube (CNT), graphene and silicon carbide nanofibers [6–9]. In general, these techniques include chemical vapor deposition (CVD) and chemical modification. CVD is one of the most frequently used approaches to modify the CFs. CVD leads to the direct growth of the CNTs onto the surface of the CF; however, the method has an important limitation that the catalyst and high temperature deposition condition destroy the surface of the CFs leading to the degradation of the mechanical properties [10]. Moreover, CFs contain a high fraction of graphitic carbon leading to its low reactivity. Alternatively, grafting CNTs onto the surface of CF through chemical reaction has also been investigated extensively. CNTs are grafted onto the surface of CFs by chemical reactions using polyhedral oligomeric silsesquioxanes, poly(amido amine), and hexamethylenediamine as coupling agents [6–9]. The chemical modification results in obvious improvement in the interfacial properties, in particular, wettability and surface energy, of the CFs. The method of chemical grafting can significantly improve the surface roughness of the CFs and is beneficial for the CFs to integrate with the polymer matrix [11–15].

Recently, graphene, which has been extensively applied in diverse areas including field effect transistors, organic solar cells,

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chemical/bio sensors, and transparent electrodes in photovoltaic devices, has attracted significant attention [16–18]. Research on graphene contributes remarkably to the advancements in material fields [19–25]. Several fascinating properties of graphene were discovered through the investigation of pristine graphene including extremely high charge mobility with 2.3% absorption of visible light, thermal conductivity, the highest strength, and the highest theoretical specific surface area. However, two critical issues are encountered which include fabrication of cost effective graphene nanostructures produced at large scale and its high efficiency because graphene sheets are difficult to be incorporated and distributed homogeneously into various matrices [26]. The solution to the above mentioned problem has been provided in terms of an attractive approach to produce low cost graphene oxide/reduced graphene oxide (GO/RGO) sheets in large quantities [27,28]. The method includes the incorporation of several groups such as hydroxyl, carboxyl, epoxy, and other similar groups, on the surface of GO. Incorporation of groups lead to the efficient combination of graphene with the matrix. Besides, the active groups provide numerous options to graft GO onto the CF by different multifunctional coupling agents and different chemical reactions.

Moreover, synthesis of polymer shows significant importance for both CFRP and its potential applications because they exhibit excellent chemical, thermal, and mechanical properties. This research mainly focuses on the preceramic polymers [29]. In the past decades, extensive research efforts have been devoted to the preceramic polymers which act as precursors for the fabrication of mainly silicon (Si)-based advanced ceramics [30]. Decomposition, crystallization, phase separation, and creep of the precursor polymers result in the formation of ceramics exhibiting excellent stability at high temperature (up to 2000 °C) [31]. Thus, the transformation of precursor polymers to the ceramics leads to the formation of polymer-derived ceramics (PDCs). Moreover, preceramic polymers owing to their multiple compositions have been used as polymer matrix to fabricate CF reinforced polymer composites. Numerous important engineering fields suitable for potential application of PDCs include high-temperature-resistant materials (energy materials, automotive, aerospace), hard materials, chemical engineering (catalyst support, food- and biotechnology), and functional materials in electrical engineering as well as in micro/nanoelectronics. Synthesis of preceramic polymers involve low temperature polymerization and cross-linking reactions, followed by pyrolysis at high temperatures (1000–1600 °C) in an inert atmosphere [32–35]. The structure and composition of monomers play an important role in controlling the composition and final structure of ceramics. Lee et al. synthesized siliconborocarbonitride (SiBCN) preceramic polymers using three monomers, trichlorosilane (HSiCl<sub>3</sub>), boron trichloride (BCl<sub>3</sub>), and hexamethyldisilazane (HMDZ), at a molar ratio of about 1:1:4. The product so-obtained exhibited an amorphous structure with cross-linked bonds during the elimination of (CH<sub>3</sub>)<sub>3</sub>SiCl. Pyrolysis of SiBCN preceramic polymers at 1600 °C converted them to ceramics via phase transformation; thus, providing hydrothermal stability under autoclave test [36]. Jansen et al. developed borazine derivative [B(CH(CH<sub>3</sub>)(SiCl<sub>3</sub>))NH]<sub>3</sub> (TSEB) using 1-(trichlorosilyl)-1-(dichloroboryl)ethane (Cl<sub>3</sub>SiCH(CH<sub>3</sub>)BCl<sub>2</sub>) with HMDZ under ambient conditions. The specially designed molecule served as a single source precursor for the synthesis of SiBCN preceramic polymers. Pursuing this philosophy, polymerization of TSEB with methylamine as the cross-linking reagent led to the fabrication of highly homogeneous preceramic polymer. The resulting amorphous SiBCN of the approximate elemental composition of Si<sub>3</sub>B<sub>3</sub>N<sub>5</sub>C<sub>4</sub> exhibited an outstanding thermal durability at 2000 °C under inert conditions and it was also stable in pure oxygen up to at least 1300 °C [37]. Bernard et al. fabricated SiBCN preceramic polymers

using two monomers, namely, dichloromethylvinylsilane (CH<sub>2</sub>=CHSiCH<sub>2</sub>Cl<sub>2</sub>) and borane dimethylsulfide (BH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>), subsequently, it was processed into polymer green fibers by a melt spinning process. Shaping processing at 200 °C followed by pyrolysis at 1400 °C in a nitrogen atmosphere resulted in the formation of the amorphous and stable Si<sub>3.0</sub>B<sub>1.0</sub>C<sub>5.0</sub>N<sub>2.4</sub> ceramic fibers with tensile strength of 1.3 GPa and Young's modulus of 170 GPa [38]. Various monomers used for synthesis of SiBCN preceramic polymers have a common characteristic, i.e., they contain active chlorine, which undergoes substitution reaction with the hydroxyl groups present on the surface of polymer matrix.

In general, prior to grafting of GO onto CFs, they are treated with concentrated nitric acid by liquid phase oxidation method, which incorporates numerous hydroxyl and carboxyl groups on the surface of CF; moreover, GO itself contains a large number of hydroxyl groups. Thus, the monomers with active chlorine can directly react with hydroxyl groups present on CF and GO. Therefore, the chlorinated compound not only acts as a monomer to synthesize the SiBCN preceramic polymers, but also chemically combines CF, GO, and SiBCN preceramic polymers as a whole by acting as an adhesive. In this study, we proposed a novel method to synthesize the SiBCN preceramic polymer on the modified CF surface by in situ polymerization. In particular, CFs grafted with GO were employed to fabricate CF-g-GO/SiBCN preceramic polymer hierarchical structure. Pyrolysis of CF-g-GO/SiBCN preceramic polymer at 1400 °C in inert atmosphere led to the formation of Si<sub>3</sub>N<sub>4</sub>/SiC/BN ceramics. The composite material exhibited good stability at high temperature.

## 2. Experimental section

### 2.1. Materials

All solvents, monomers, and other chemicals were purchased from Aldrich unless otherwise stated. CF (Jiangsu tianniao Company, China) had an average diameter of 7 μm. In this study, following chemicals were employed: (3-aminopropyl)triethoxysilane (99%), (3-glycidyloxypropyl)trimethoxysilane (98%), boron trichloride solution (BCl<sub>3</sub>, 1.0 M in methylene chloride), trichlorosilane (HSiCl<sub>3</sub>, 99%), and hexamethyldisilazane (HMDZ, 99.9%). GO was synthesized according to the literature methods [28]. Other chemicals were of analytical grade and used as received.

### 2.2. Preparation of GO amine

GO was fabricated according to the modified Hummers' method. In a typical synthesis, GO was taken in a round bottomed flask and dispersed in ethanol (100 mL) for 1 h. Subsequently, (3-aminopropyl)triethoxysilane in deionized water was added to the stirring reaction mixture. The reaction mixture was heated to 60 °C for 24 h. Later, the contents were cooled to room temperature and the solvent was removed by centrifugation. The so-obtained solid product was dried under vacuum until constant weight was obtained; thus, leading to the formation of GO amine.

### 2.3. Grafting of GO onto CF (CF-g-GO)

CF was added to acetone with magnetic stirring at 70 °C for 48 h, filtered, and thoroughly washed with acetone. CF was dried under vacuum, and dried CF and concentrated nitric acid were taken in a round bottomed flask. The mixture was stirred at 80 °C for 3 h. The solid products were dried under vacuum until constant weight was obtained. GO amine (0.5 g) was dispersed by ultrasonication for 2 h in dimethylformamide (DMF, 100 mL) taken in a round bottomed flask. Subsequently, acidified CF was added and the reaction

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