

Surface Modification of Carbon Fibres for Interface Improvement in Textile Composites

Jiawen Qiu¹ · Jiashen Li¹ · Zishun Yuan¹ ·
Haoxian Zeng^{1,2} · Xiaogang Chen¹ 

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Abstract The performance of carbon fibre-reinforced composites is dependent to a great extent on the properties of fibre-matrix interface. In this research, based on the reviewed surface modification technique and inspired by the in situ growth of three-dimensional graphene coatings on nanomaterials, a new method of in situ growth of a graphene-related structure on the surface of carbon fibres is to be applied, for which it is intended to use a mixed solution of Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and D-Glucose monohydrate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$) to treat the carbon fibres under specific conditions to in-situ growth of a graphene-related coatings on the surface of carbon fibres. Firstly, the method was carried out by heating the mixed solution under specific temperature on the silicon wafer substrate and followed with characterisation experiments such as Raman and Scanning Electron Microscopy (SEM). Then, the mixed solution was applied on the carbon fibres and treated under the same condition. The characterisation results indicated successfully growth of the porous carbon coatings on the surface of the carbon fibres, which contained with graphene-related structures, while other characterization experiment like Transition Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS) will need to be used to further characterise the porous carbon structure. The interfacial shear strength between the fibre and the porous carbon coating also need to be characterised by using the micro-bond test.

Keywords Carbon fibre modification · Graphene · Composites · Characterisation · Interface

1 Introduction

Carbon fibres reinforced composites have the superior stiffness to weight and strength-to-weight ratios, which have been used in a large number of high-performance structural

✉ Xiaogang Chen
xiaogang_chen@hotmail.com

¹ School of Materials, University of Manchester, Manchester M13 9PL, UK

² School of Science, Zhongyuan University of Technology, Zhengzhou, China

applications such as the automotive, aerospace, military defence and new energy [1]. Properties of fibre reinforced composites are affected by the interface between fibres and matrix [2]. Fibre-matrix interfacial adhesion is extremely important since carbon fibres have chemical inertness and poor wettability with most of the polymeric matrices [3].

The interface between the fibre and the matrix of composites materials is a very important aspect of the mechanism, which can affect the load transfer characteristics and mechanical behaviour under external loading. The wetting, dispersion and interface adhesion between fibre and matrix are key factors in designing fibre reinforced composites [4–6]. Studies in the effect of chemical vapor deposition (CVD) grafting on the mechanical properties of carbon/epoxy composites started decades ago. The synthesis of 3D graphene layers on non-metal substrates by using the CVD method also has been accomplished [7–9]. In continuous fibre-reinforced composites, the load is transferred from the matrix to the fibre through shear. With poor interfacial strength, shear stress is not able to be transferred to the fibre effectively, thus creating a weaker and less efficient composite [3]. The commercial carbon fibres are coated with a thin layer of epoxy resin, which is used to improve the handling and to decrease damage during processing and handling [3]. Removal of commercial sizing can also improve the surface chemical reactivity, which is beneficial to the enhancement of the fibre/resin interface, and make the catalyst precursors and carbon sources locate on the carbon fibre easily [10]. Zhang et al. have used acetone to treat the carbon fibre to remove the commercial size from the surface of the carbon fibre [2]. In the study by Li et al. they used 65 wt% HNO_3 to remove the size and also to introduce some carboxyl groups on to the carbon fibre [11].

Inspired by the in situ growth of three-dimensional graphene coatings on nanomaterials [7, 12–15], this paper proposes a method of in-situ growth of graphene-related structure on the surface of carbon fibres, aiming for the improvement of the fibre/resin interface. A mixed solution of a catalyst, ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and a carbon source, D-glucose monohydrate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$), is used to treat the carbon fibres, before Heating the treated carbon fibres in a tube-furnace under specific conditions to in-situ grow a graphene-related coating on the surface of carbon fibres. The in-situ growth of graphene-related coating is believed to be able to improve the interface adhesion between the carbon fibre and the resin.

2 Experimental Section

2.1 Materials

The carbon fibres used in this research were 12 K A-42 DowAksa (Turkey), and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and D-glucose monohydrate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$) were purchased from Fisher Scientific and Sigma-Aldrich® (UK) respectively. The nitric acid (HNO_3) and acetone (CH_3COCH_3) were also purchased from Sigma-Aldrich® (UK).

2.2 Methodology

Qian et al. [16] used the chemical vapour deposition (CVD) method to grow carbon nanotubes on carbon fibres. Iron was selected as the catalyst and pre-deposited on carbon fibres directly for the formation of carbon nano-tubes (CNT). Small holes were observed on some fracture surfaces of the CNT-grafted fibre composites and the formation of the pits was attributed to “the dissolution of iron into the carbon fibres” at the reaction temperature [13], leading to

weakened carbon fibres. Also based on the CVD methods, Zhang et al. [7] constructed in-situ 2D graphene sheets on the bulk metal substrates by introducing a trace amount of transition metal salts and solid carbon sources with strictly controlled content and ratio.

In the design of this experiment, iron and an extra carbon source material are coated to carbon fibres, so that the extra carbon source can help to restrict the iron particles to a small size. The iron particles near the carbon fibre dissolve carbon atoms both from the carbon fibre and the extra carbon source at high temperature. When the temperature decreases, carbon atoms are released from the iron particles and they form graphene-related layers. Thus, these graphene-related layers are grown in-situ and have primary contact with the carbon fibres as shown in Fig. 1. C-C bonds are expected between the graphene-related structure and the carbon fibres, but not other chemically grafted GO with covalent bonds [11], which cannot survive high temperature during the following CVD process. It is envisaged that the interface strength between the carbon fibre and the graphene created in this research are increased. In order to achieve the best condition of growing graphene-related coatings on the surface of carbon fibres, the preliminary experiments were carried out on a silicon wafer substrate firstly before applying on the carbon fibres.

3 Growth of Graphene-Related Coatings

The mixed solution, made by dissolving ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as the catalyst precursor and glucose monohydrate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$) as the carbon source into deionized water at a weight ratio of 1:10:16, was used to coat the carbon fibre [7, 13], aiming at the in-situ growth of porous carbon structures on the surface of carbon fibres. In order to exclude the possible effects of commercial sizing on the interfacial shear strength and to improve the uniformity of the porous

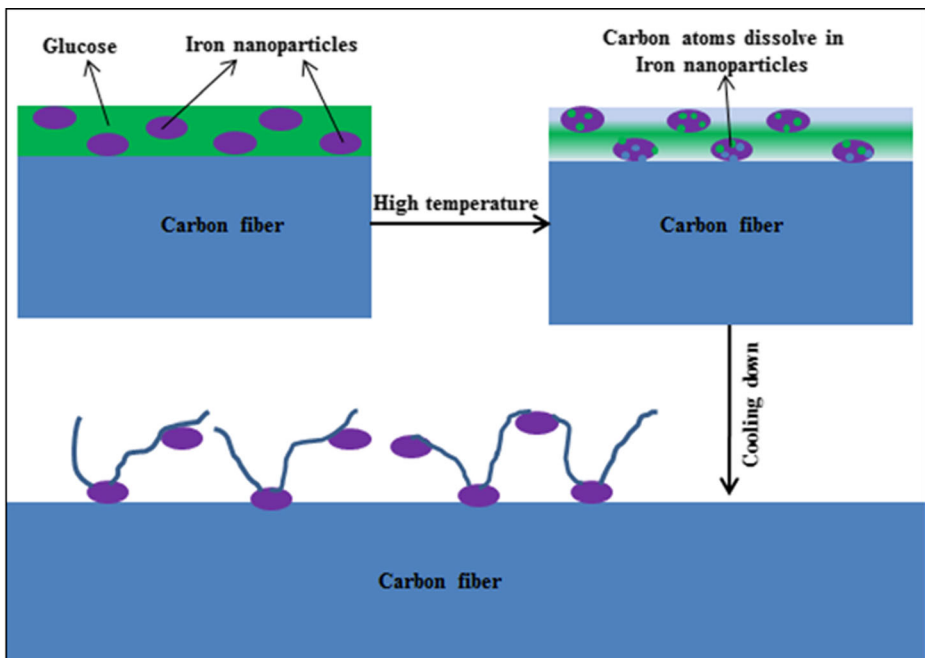


Fig. 1 The methodology of in-situ growth of graphene-related coatings on the surface of carbon fibres

carbon coating, the size on the fibre surface was removed using two different methods following the practice used by other researchers [2, 11]. Using the first method, the carbon fibres were immersed into 65 wt% HNO_3 for 1.5 h. Another method allows the carbon fibres to be immersed in acetone solution for 48 h. After the removal of the size from the carbon fibre surface, the carbon fibres were fully immersed into the mixed solution mentioned above before drying the fibres in an oven at 80°C for 12 h. Then the samples were then transferred to the tube furnace with the protection of Ar/H_2 gas in a (95:5) ratio atmosphere. The maximum temperature was raised to 950°C at a rate of $5^\circ\text{C}/\text{min}$ and maintained for 6 h according to the findings in previous studies [7, 13–15]. Finally, the sample was cooled down to room temperature. This process is illustrated in Fig. 2.

4 Characterisation of Results and Discussions

4.1 Characterisation of the Modified Method from Using Silicon Substrate

The weight ratio between the ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and D-glucose monohydrate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$) and the heating temperature was decided through the preliminary experiments using silicon wafer as the substrate. The growth of the graphene is controlled by changing the heating temperature, heating time, and the ratio of carbon source to catalyst. Based on the preliminary experiments on forming grapheme on silicon substrate, the optimal conditions for graphene growth are 950°C as the maximum temperature, 6 h heating time at the maximum temperature, and 10:1 ratio between the carbon source and the catalyst precursors. The solution on the silicon substrates was heated in the tube furnace under high temperature and an Argon/H_2 atmosphere. Then the residues of the reacted solution were characterised by using scanning electron microscopy (SEM/Ultra 55) and Raman spectroscopy (Renishaw 1000 514 nm Argon-ion laser). The SEM results demonstrated that a porous carbon structure have been generated from the residues of the solution as shown in Fig. 3a and b. The dotted structure distributed in the porous carbon structure was shown by SEM to be iron and the rest of the material is carbon under the Energy-dispersive X-ray Analysis (EDS) mode

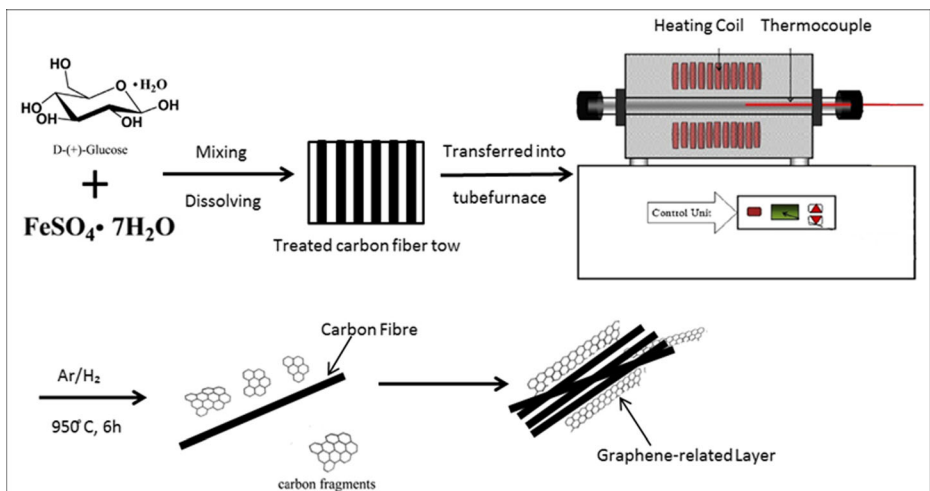


Fig. 2 The experiment of in-situ growth of graphene-related coatings on the surface of carbon fibres

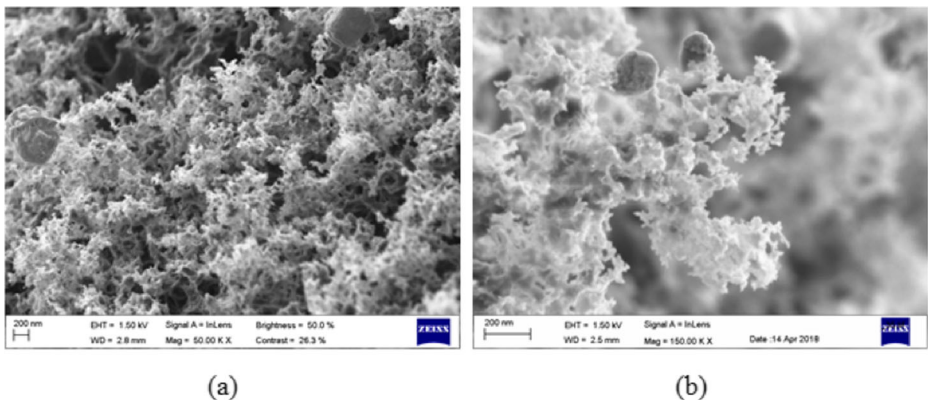


Fig. 3 a and b The porous carbon structure generated from the reacted Ferrous Sulfate Heptahydrate and D-glucose monohydrate mixed solutions

shown in Fig. 4a, b and c. There should be graphene-related structures generated in the porous carbon structures according to the achieved Raman spectrum results.

The Raman spectrum Fig. 5 indicated that it consists of two prominent peaks at around ~ 1330 and ~ 1600 cm^{-1} along with a wide band extending from about $2600\text{--}3200$ cm^{-1} . The peaks at ~ 1330 and ~ 1600 cm^{-1} are the D and G bands respectively [17, 18]. The G band is a characteristic of all graphitic structures. The D band is attributed to the presence of defects, wrinkle formation and the presence of functional groups [19, 20]. The wide band at the high frequency end of the spectrum contains three peaks around 2650cm^{-1} , 2930 cm^{-1} and 3190 cm^{-1} , respectively. The peak at ~ 2650 is known as the 2D band since it is an overtone of the D band. While unlike the 2D peak of the perfect monolayer graphene which has high intensity and a lorentzian shape, the 2D peak indicated a few layered graphene depositions, and is complex in shape and evolves with the number of layers [21].

4.2 The Effect of the Desizing with Different Method

The changes in surface topography for the carbon fibres after different treatment methods were verified by SEM analysis. The darker areas along the fibre axis can be seen on the surface of commercial fibre as shown in Fig. 6a. After removing the commercial sizing by using acetone and HNO_3 , the desized carbon fibre with no darker areas can be observed and the longitudinal grooves on the surface of carbon fibres were exposed and no obvious damage was observed as illustrated in Figs. 6b and c, apart from the exposed longitudinal grooves on the surface of the

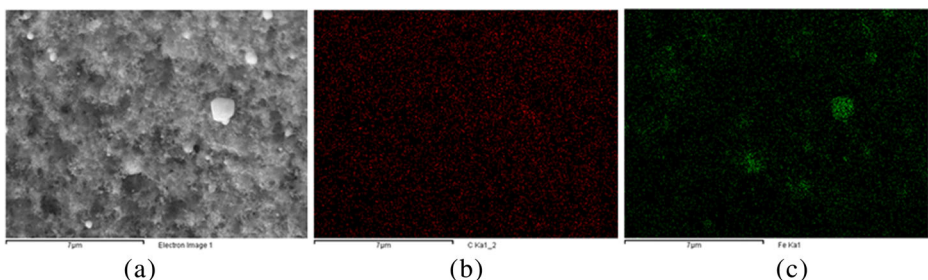


Fig. 4 a The SEM image of the porous carbon structure b The C element in the porous carbon structure under the EDS mode of the SEM c The Fe element distribution in the porous C carbon structure under the EDS mode of the SEM

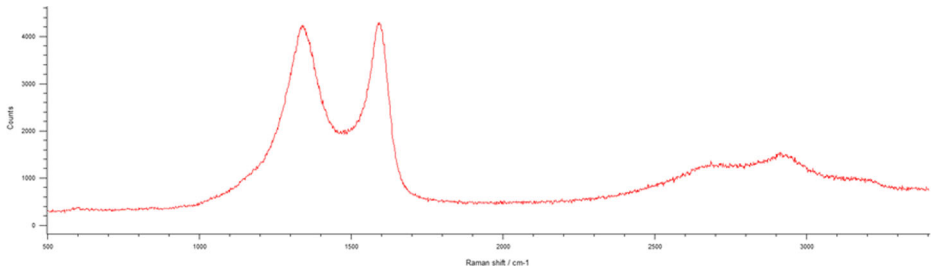


Fig. 5 Characterisation results of the residues of the reacted Ferrous Sulfate Heptahydrate and D-glucose monohydrate mixed solutions analysed by using Raman spectroscopy

carbon fibres. Tensile test was also carried out to verify the damage caused by removing the size from the carbon fibre. 20 tests were carried out for sized and desized carbon fibres. It was found that the tensile strength of the carbon fibres desized using acetone and HNO_3 reduced 7 and 5% respectively compared to the commercial carbon fibres.

4.3 In-Situ Growth of Graphene on Carbon Fibres

The raw carbon fibre treated with solution and then heated in the tube-furnace are shown in Fig. 7a and indicated that there is only small amount of porous carbon structure coating was

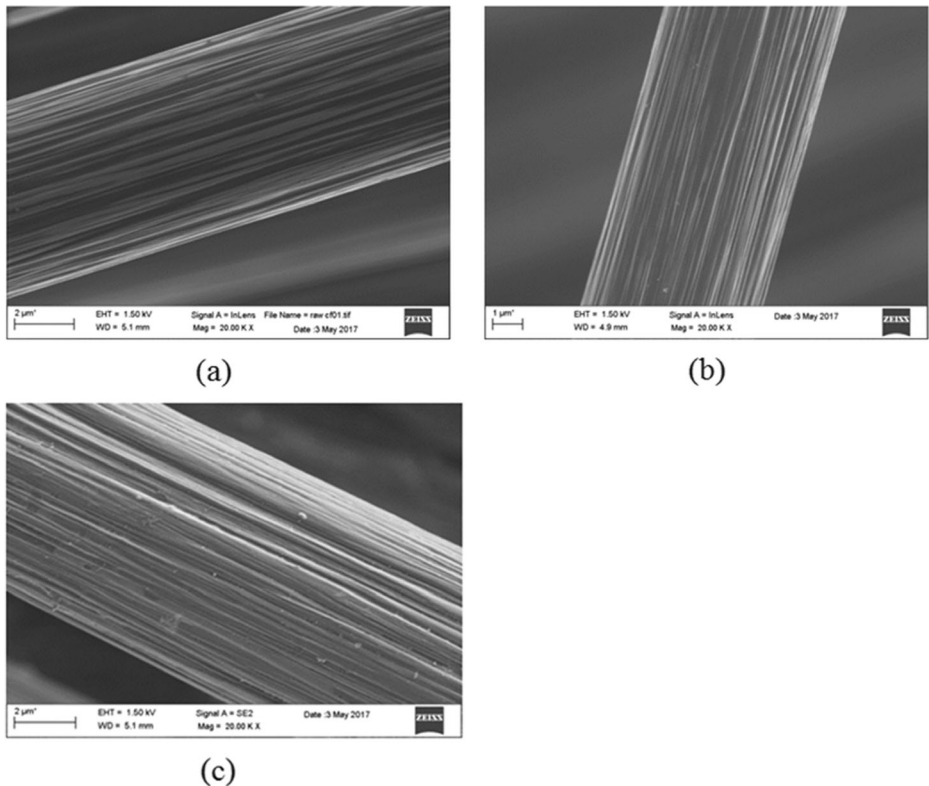


Fig. 6 a Raw carbon fibres b Desized carbon fibres by using Acetone c Desized carbon fibres by using HNO_3

grown on the surface of the sized carbon fibres. A more uniform coating was grown on the surface of the desized carbon fibres as shown in Fig. 7b and c. This is caused by the sizing on surface of the carbon fibres that lead to the uneven of the solution on the surface of carbon fibres. The longitudinal grooves on the surface of the carbon fibre after treating by HNO_3 and Acetone can help to load the solution better compared with the raw carbon fibre [10].

5 Conclusion

The preliminary experiment results that characterised by Raman spectroscopy shown that there are three peaks at around $\sim 1330\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$ along with a wide band extending from about $2600\text{--}3200\text{ cm}^{-1}$, which indicated there should be graphene layers in the porous carbon structure. However, different characterisation methods such as TEM and XPS also should be used to help to produce incontrovertible results.

The SEM image demonstrated that the raw carbon fibres treated with mixed solution samples have the worst coating compared with the desized samples, which indicated that the commercial sizing does affect the uniformity of the graphene-related coatings. Thus, the commercial sizing needs to be removed to reduce the effect on the growth of the graphene-related layer on the surface of the carbon fibres. In addition, the tensile property of the carbon

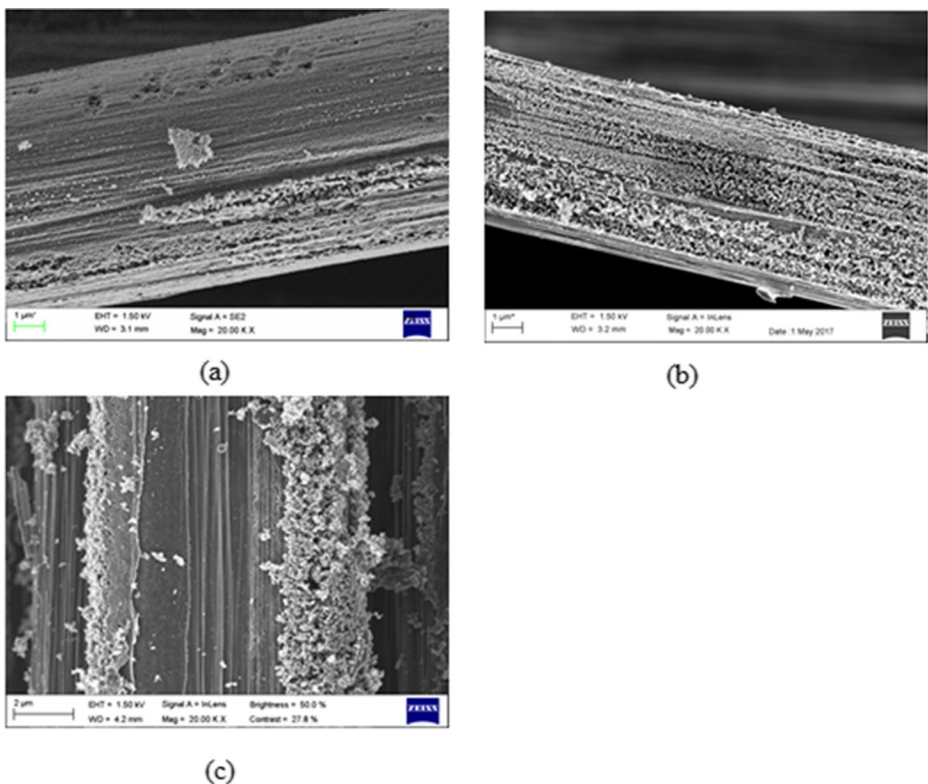


Fig. 7 a Raw carbon fibre treated with Ferrous/glucose solution b Desized carbon fibre (with Acetone) and treated with Ferrous/glucose solution c Desized carbon fibre (with HNO_3) and treated with Ferrous/glucose solution

fibre have not been affected too much after size removal from the carbon fibre, which have reduced 7 and 5% respectively by using acetone and HNO₃.

The graphene-related coatings have been in-situ grown on the surface of the carbon fibres but more characterisation methods need to be applied to characterise the bonding between the generated coatings and the carbon fibre. On the other hand, the composite will need to be manufactured to identify the property of the modified carbon fibre reinforced composites.

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